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Level I - Preliminary

JRB Associates, Inc.,
McLean, VA

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16. ABSTRACT

The purpose of the Level I materials balance for 1,2 dichloroethane (EDC) is to evaluate the sources of release of EDC to the environment. EDC is produced via direct chlorination and oxychlorination of ethylene. EDC is used consumptively in the production of other chemicals such as vinyl chloride, monomer, perchloroethylene, trichloroethylene, ethyleneamines and vinylidene chloride. EDC is also used in the production of leaded gasoline additives as lead scavenger. Releases of EDC from the production and consumptive uses appear to be the major sources of EDC emissions.

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FINAL DRAFT

LEVEL I MATERIALS BALANCE:

1,2-DICHLOROETHANE

Prepared for:

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OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
SURVEY AND ANALYSIS DIVISION
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Submitted: February 8, 1980

THE FINAL REPORT PRESENTED HEREIN RESULTED FROM A LEVEL I MATERIALS BALANCE STUDY ON 1,2-DICHLOROETHANE. THE RESULTS WERE BASED ON AN ANALYSIS OF LITERATURE SUPPLIED BY EPA. ALTHOUGH SUPPLEMENTARY INFORMATION UNDOUBTEDLY EXISTS, OBTAINING IT WAS OUTSIDE THE SCOPE OF THIS TASK. THE LEVEL I REPORT IS INTENDED TO SERVE AS A FOCUS OF DISCUSSION AND AS A BASIS FOR FUTURE MATERIALS BALANCE STUDIES: IT IS NOT MEANT TO BE A DEFINITIVE STUDY.

LEVELS OF ENVIRONMENTAL MATERIALS BALANCES

Materials balance studies are performed at three levels or depths of study and effort. In general the study of a chemical proceeds sequentially through these three levels. Particular chemicals are assigned to be studied at one of the levels on the basis of availability of information. The three levels are described below:

Level I:

A LEVEL I MATERIALS BALANCE requires the lowest level of effort and involves a survey of readily available information for constructing the materials balance. Ordinarily, many assumptions must be made in accounting for gaps in information; however, all are substantiated to the greatest degree possible. Where possible the uncertainties in numerical values are given, otherwise they are estimated. Data gaps are identified and recommendations are made for filling them. A Level I materials balance relies heavily on the EPA's Chemical Information Division (CID) to provide readily available information. The first draft of most Level I Materials Balances is completed within a three to six week period; CID literature searches are generally completed within two weeks. Thus the total time required for preparation of the initial draft of a Level I materials balance ranges from five to eight weeks.

Level II:

A LEVEL II MATERIALS BALANCE involves a greater level of effort, including an in-depth search for all information relevant to the materials balance. The search includes all literature (concentrating on primary references), contacts with trade associations, other agencies, and industry to try to uncover unpublished information, and possibly site investigations. Uncertainties and further data needs are identified in the Level II report. Recommendations for site sampling needs for Level III are also identified.

Level III:

A LEVEL III MATERIALS BALANCE generally involves the assimilation of new data obtained. It builds on the Level II literature searches and reviews of industrial production data by filling in data gaps through site visits and monitoring. The data generated for a Level III Materials Balance are intended to be statistically valid and have known confidence values. Level III Materials Balances are also intended to provide a basis for regulations or legal proceedings.

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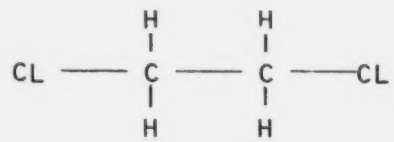
EXECUTIVE SUMMARY

General Description of 1,2-Dichloroethane

1,2-Dichloroethane is a synthetic organic compound with the following chemical structure:



The common name for this compound is ethylene dichloride (EDC). It is a colorless, oily liquid with a sweet taste and an odor similar to that of chloroform. EDC has a density of 1.2351 and is very volatile (vp=62.5 mm Hg at 20°C). It is a powerful solvent for unvulcanized rubber, fats, greases, waxes, resins and many other organic compounds. EDC is only slightly soluble in water, but is completely miscible with most of the usual organic solvents. Vapors from EDC burn readily in air, but the liquid burns poorly with a smoke flame. Bulk quantities of the compound are stable when kept dry at room temperature, but the material undergoes slow decomposition when exposed to air, moisture and light.

Unlike some other chlorinated hydrocarbons (namely, DDT and PCB), EDC does not appear to accumulate in the environment. The material evaporates rapidly from water into the atmosphere, where photo-oxidation appears to be the main destructive mechanism. However, EDC is toxic to humans following oral, respiratory or skin and mucous membrane absorption.

Production and Primary Uses

Of all the chlorinated organic compounds manufactured in the United States, EDC is produced in the greatest quantity. The U.S. production figure for 1977 is 4.99 million metric tons. Figures are not yet available for 1978 but are expected to have escalated by about 4%. The major use of EDC is as a raw material for the production of vinyl chloride monomer and other chlorinated hydrocarbons. The breakdown statistics for the use of EDC in these production processes is shown in Table 1.0.

Summary of Materials Balance of EDC

Of the 5.05 million kkg of EDC actually produced in the U.S. in 1977, a total of 6.7×10^4 kkg or about 1.4% of that produced) is estimated to have been released to the environment. Of this total, 5.4×10^4 kkg (88%) is estimated to have been released to the air; 190 kkg (0.3%) to water; an insignificant amount to land; and 1.3×10^4 kkg was destroyed by incineration. This estimate is based on little available information and should be verified in later studies. The remaining 4.99 million kkg is either exported, destroyed via combustion processes, or chemically bound in the products made from EDC, including other chemicals. Figure 1.0 shows the flow of EDC from the production to the use phase, the environmenta releases associated with each phase, and the materials balance. The materials balance is based on the 1977 data, since production figures were not yet available for 1978. Most of EDC releases occur during production processes. The releases associated with the manufacture of EDC are close to 4.12 kkg, or 61% of the total release of EDC to the environment.

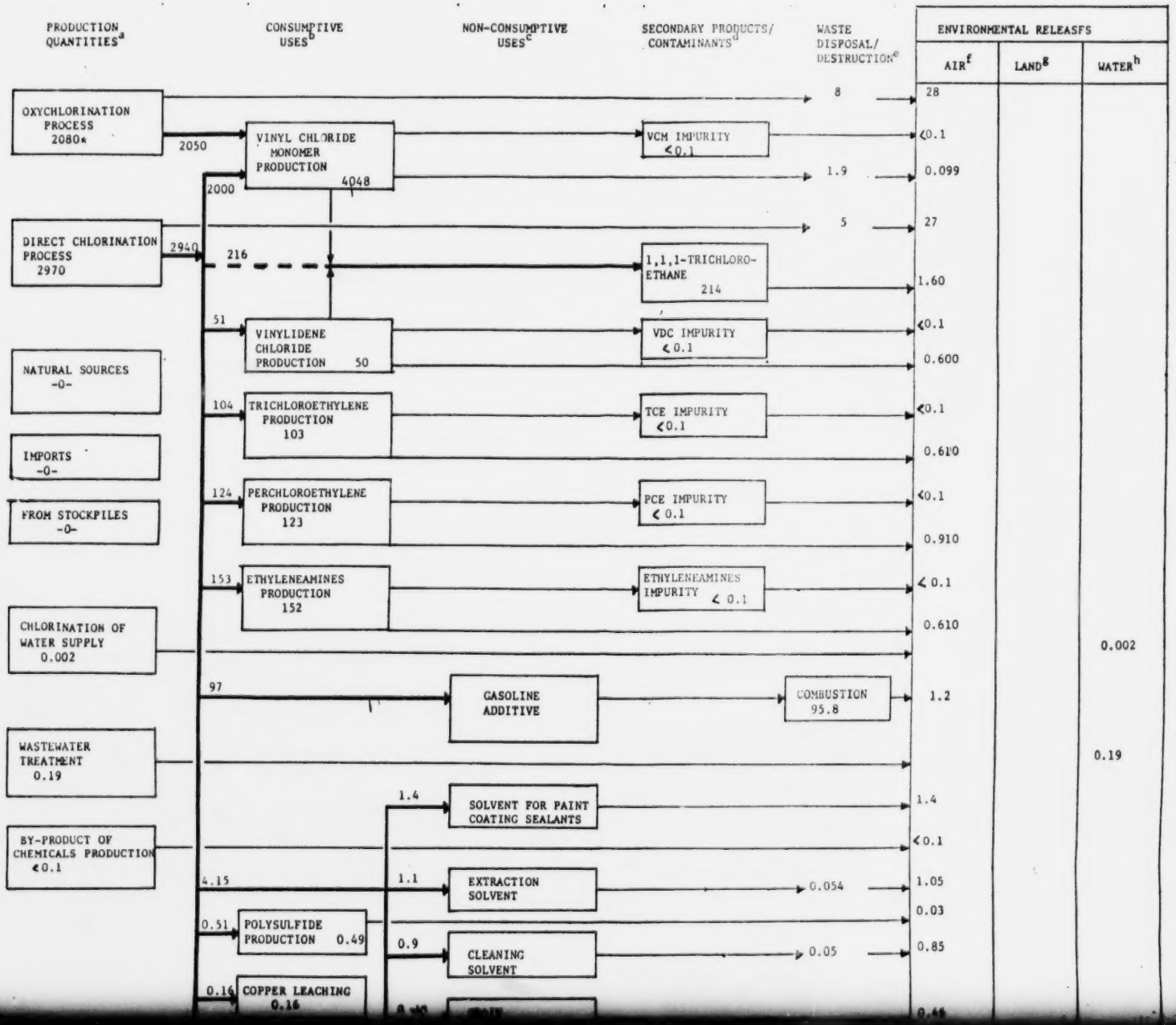
The third most important group of releases occur during the manufacturing processes which utilize EDC as a feedstock (e.g., the production of vinyl chloride monomer, trichloroethylene, polysulfide rubber, etc.). For these manufacturing processes, most of the emissions are released directly to the atmosphere (60%), but some EDC is associated with various sludges that are generated. Total emissions from this source are estimated at 5600 kkg. From the total amount of EDC used as

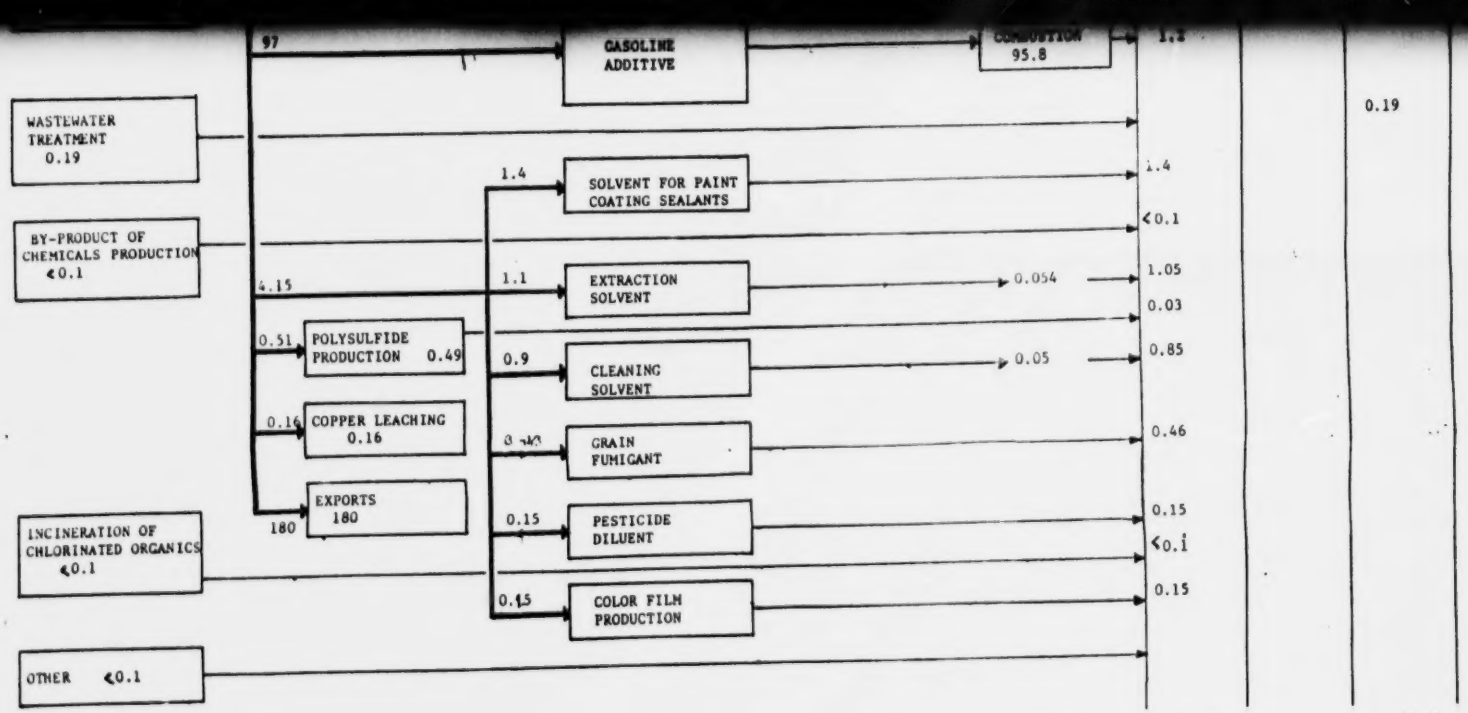
lead scavenger (9.7×10^4 kkg), EDC emission to the environment was estimated at 1200 kkg (or 18% of the total EDC emission). The remaining quantity ($9.6\% \times 10^2$ kkg) was estimated to have been destroyed by the combustion process.

TABLE 1.0 SUMMARY OF USES OF EDC

USE	AMOUNT OF EDC USED (KKG)	PERCENT OF TOTAL
VINYL CHLORIDE MONOMER PRODUCTION	4.1×10^6	82%
METHYL CHLOROFORM PRODUCTION	2.2×10^5	4%
ETHYLENEAMINE PRODUCTION	1.5×10^5	3%
PERCHLOROETHYLENE PRODUCTION	1.2×10^5	2%
TRICHLOROETHYLENE PRODUCTION	1.0×10^5	2%
ADDITIVE TO GASOLINE	9.6×10^4	2%
VINYLIDENE CHLORIDE PRODUCTION	5.3×10^4	1%
TOTAL OF MAJOR USES	4.8×10^6	96%
FORMULATION OF PAINTS, COATINGS, AND ADHESIVES	1.4×10^3	< 1%
EXTRACTION SOLVENT	1.1×10^3	< 1%
CLEANING SOLVENT	9.1×10^2	< 1%
POLYSULFIDES MANUFACTURE	5.2×10^2	< 1%
GRAIN FUMIGATION	4.6×10^2	< 1%
MISCELLANEOUS	4.6×10^2	< 1%
TOTAL OF MINOR USES	4.8×10^3	< 1%
EXPORTS	1.8×10^5	3.6%
GRAND TOTAL (MAJOR USES + MINOR USES + EXPORTS) =	5.0×10^6	100%

All Units: 10^3 kkg/year





TOTAL: (5050) (4477) (0) (214) (111) (66.8) (0.2)

*Figure not exact due to rounding off.

Summary of Materials Balance:

Amount Produced (5050 kkg) = amount consumed as primary products (4477 kkg)

+ amount consumed as secondary products (214 kkg)

+ amount exported (180 kkg)

+ amount in stockpile and in use (0 kkg)

+ amount present in waste piles, landfills, etc. (0 kkg)

+ amount destroyed by incineration (111 kkg)

+ amount released to air (66.8 kkg)

+ amount released to water (0.3 kkg)

+ amount released to land (0 kkg)

a - Production quantities include: imports, natural production, stockpiles from previous years, by-products of industrial processes, production as a result of the use of precursors, and any processes which result in the formation of EDC.

b- Amount of EDC actually consumed as an intermediate in the production of the chemicals listed below. This amount is calculated by subtracting the environmental releases of EDC from the input of EDC. This amount excludes exports of EDC. A separate calculation is made in this case.

c- Amount of EDC that is not used as an intermediate in the production of other chemicals. This amount is estimated to be zero because EDC is totally released to the environment when present in the below listed products.

+ amount exported (180 kkg)

+ amount in stockpile and in use (0 kkg)

+ amount present in waste piles, landfills, etc. (0 kkg)

+ amount destroyed by incineration (111 kkg)

+ amount released to air (66.8 kkg)

+ amount released to water (0.3 kkg)

+ amount released to land (0 kkg)

a - Production quantities include: imports, natural production, stockpiles from previous years, by-products of industrial processes, production as a result of the use of precursors, and any processes which result in the formation of EDC.

b- Amount of EDC actually consumed as an intermediate in the production of the chemicals listed below. This amount is calculated by subtracting the environmental releases of EDC from the input of EDC. This amount excludes exports of EDC. A separate calculation is made in this case.

c- Amount of EDC that is not used as an intermediate in the production of other chemicals. This amount is estimated to be zero because EDC is totally released to the environment when present in the below listed products.

d- Amount of EDC present as a contaminant or used as an intermediate in formation of secondary products. This amount is calculated by subtracting the environmental releases of EDC from the input of EDC.

e- Amount of EDC destroyed by incineration (in this case apparently no waste is deposited in landfills.

f- Amount of EDC released to air.

g- Amount of EDC released to land. Includes land spreading and spraying but does not include wastes in landfills as a release to land.

h- Amount of EDC released to water. Includes releases to water from landfills.

FIGURE 1.0 ENVIRONMENTAL MATERIALS BALANCE FOR EDC (1977)

1.0 INTRODUCTION

This report presents the results of a Level I Environmental Materials Balance for 1,2-dichloroethane (EDC). The study was conducted for the Survey and Analysis Division of the U.S. EPA Office of Pesticides and Toxic Substances (OPTS). The primary objective of the study was to estimate within the constraints of time and information availability, the quantity of EDC released to the environment annually, the sources and locations of these emissions, and the form in which EDC is released.

By definition, a Level I materials balance involves a survey of readily available information supplied mostly by the Chemical Information Division of OTS. In a Level I study many assumptions and estimations must be made in accounting for all releases of the chemical to the environment. The results are based on all the assumptions presented and represent the best analysis of the currently available data.

The following pages present the findings of this study. Section 2.0 explains the production of EDC and examines all releases of EDC to the environment during these processes. Section 3.0 describes the releases related to all end products and uses of EDC following its production. A summary of all the environmental releases of EDC is presented in Section 4.0. Section 5.0 is a detailed review of the disposal and destruction of EDC. The uncertainties of the estimates presented in the report are summarized in Section 6.0. The final section of the report, Section 7.0, identifies the gaps in the available data. The appendix provides supplementary information which substantiates some of the conclusions drawn in this report.

2.0 ENVIRONMENTAL RELEASE ASSOCIATED WITH THE PRODUCTION OF EDC

The sources of EDC in the United States are (1) direct production for either captive or dispersive uses, (2) indirect or inadvertent production via other processes, and (3) stockpiles of EDC produced in previous years. There are no imports of EDC to the United States.

2.1 ENVIRONMENTAL RELEASE OF EDC ASSOCIATED WITH DIRECT PRODUCTION PROCESSES

Direct production of EDC is accomplished in industry primarily through the direct chlorination of ethylene or oxychlorination of ethylene. In the United States, 11 manufacturers in 17 production facilities produce EDC. Figure 2.1 shows the locations of the plants.

In 1977, 4.99 million kkg of EDC was produced in the United States (USITC, 1978). This quantity represents only that amount reported to the USITC by the manufacturers. Because of reporting problems in earlier years, there were discrepancies in quantities reported to have been manufactured and quantities reported to have been used. Therefore, an independent method was used to check the accuracy of the USITC data for 1977.

This method is based on the following equation:

Total EDC Produced = (Total EDC Used in Major Uses) + (Total EDC Used in Minor Uses) + (EDC Exports) + (Stockpiles)

The first step, determining the amount of EDC necessary to produce the major chemicals, can be found in Section 3.0. By adding all the quantities calculated, 4.82×10^6 kkg is obtained. By adding the total of minor uses and exports to this quantity, the total production figure is calculated as follows:

(1) Allied Chemical Co., Baton Rouge, Louisiana
(2) Conoco Chemicals, Lake Charles, Louisiana
(3) Diamond Shamrock Corp., Deer Park, Texas
(4) Dow Chemical Co., Freeport, Texas
(5) Dow Chemical Co., Oyster Creek, Texas
(6) Dow Chemical Co., Plaquemine, Louisiana
(7) Ethyl Corp., Baton Rouge, Louisiana
(8) Ethyl Corp., Houston, Texas
(9) B.F. Goodrich Co., Calvert City, Kansas
(10) PPG Industries, Inc., Lake Charles, Louisiana
(11) PPG Industries, Inc., Guayanilla, P.R.
(12) Shell Chemical Co., Deer Park, Texas
(13) Shell Chemical Co., Norco, Louisiana
(14) Stauffer Chemical Co., Long Beach, California
(15) Union Carbide Corp., Taft, Louisiana
(16) Union Carbide Corp., Texas City, Texas
(17) Vulcan Materials Co., Geismar, Louisiana

FIGURE 2-1. LOCATIONS OF PLANTS MANUFACTURING EDC

100% of total production = Exports (3.7% of total production) + Minor Uses (0.1% of total production) + Major Uses (4.82×10^6 kkg) + Stockpiles (0)

$$\text{Total Production} = \frac{4.82 \times 10^6 \text{ kkg}}{96.2\%}$$

$$= 5.01 \times 10^6 \text{ kkg}$$

Since no significant variation exists between the two figures obtained, the quantity reported to the USITC, 4.99×10^6 kkg, is used throughout this report.

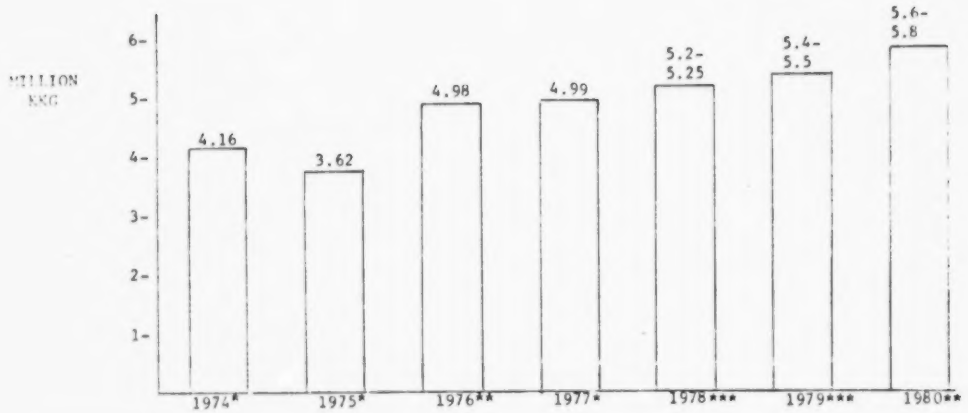
Table 2.1 lists the producers, plant locations, annual capacity, estimated production, and respective production methods for EDC. Based on current and projected markets for EDC, it has been established that annual production will rise between 4% and 5% each year through 1981; production in 1981 is expected to be approximately 6.06 million kkg (Chemical Marketing Reporter, 1977b). The production trends since 1974 are shown in Figure 2.2.

2.1.1 Release of EDC Associated With the Direct Chlorination Process

Approximately 59%, or 2.94×10^6 kkg of EDC manufactured by industry in 1977 was produced by the direct chlorination of ethylene in the presence of an $FeCl_3$ catalyst (EPA, 1979a). The chemical reaction involved in this process is presented below (McPherson, 1979):

$$Cl_2 + CH_2 = CH_2 \xrightarrow{FeCl_3} ClCH_2CH_2Cl$$

A detailed discussion of the direct chlorination process is shown in Appendix B. The production is represented diagrammatically in Figure 2.3.



*Based upon data from USITC, 1974-1977.

**Based on estimate in Mannsville Chemical Products Report, April, 1977. Chemical Products Synopsis - Ethylene Dichloride. Mannsville, New York.

***Estimates based upon 4-5% annual growth rate, as reported in Chemical Marketing Reporter, 1977b.

FIGURE 2.2 PRODUCTION TRENDS FOR EDC

TABLE 2.1 PRODUCERS OF EDC (1977)

Producer	Location	Annual Capacity (million kkg)	Estimated[a] 1977 Production (million kkg)	Production Method[b]	
				Direct Chlorination (%)	Oxychlorination (%)
Allied Chemical Corp.[c]	Baton Rouge, LA	0.272	0.214	66.7	33.3
Continental Oil Corp.	Lake Charles, LA	0.544	0.428	49.2	50.8
Diamond Shamrock Chem. Co.	Deer Park, TX	0.145	0.114	35.8	64.2
Dow Chemical Co., U.S.A.	Freeport, TX	0.726	0.571	57.1	42.9
	Oyster Creek, TX	0.499	0.392		
	Plaquemine, LA	0.590	0.464	51.7	48.3
Ethyl Corp.	Baton Rouge, LA	0.318	0.250	52.7	47.3
	Houston, TX	0.144	0.113	100.0	0.0
B.I. Goodrich Chemical Co.[d]	Calvert City, KY	0.454	0.357	33.3	66.7
PPG Industries, Inc.[e]	Lake Charles, LA	0.585	0.460	77.2	22.8
	Guayanilla, PR	0.485	0.381		
Shell Chemical Co.	Deer Park, TX	0.635	0.499	66.2	33.8
	Norco, LA	0.544	0.428		
Stauffer Chemical Co.	Long Beach, CA	0.141	0.111	69.2	30.8
Union Carbide Corp.	Taft, LA	0.068	0.053	100.0	0.0
	Texas City, TX	0.068	0.053	100.0	0.0
Vulcan Material Co.	Geismar, LA	0.159	0.125	0.0	100.0
TOTAL		6.35	4.99		

[a] Based upon 4.99 million kkg total production (78.6% of annual capacity in 1977), the production for each facility was estimated by applying 78.6% to each plant's capacity.

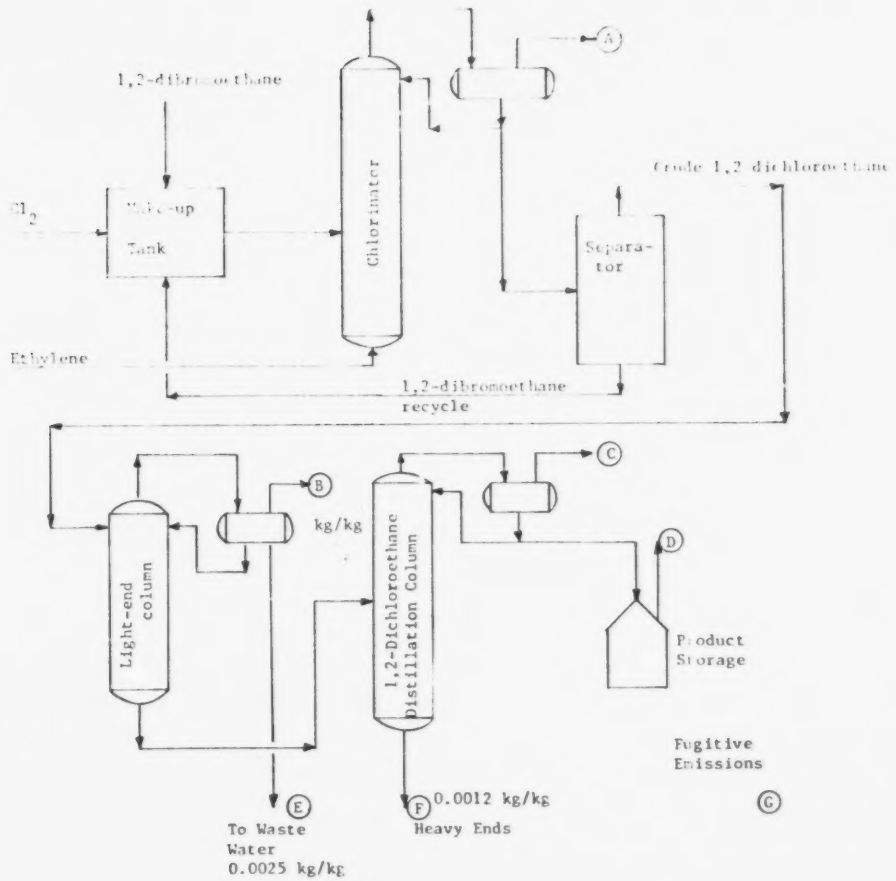
[b] Based on 1974 data (Pervier et al., 1974)

[c] In July 1978, Allied Chemical disclosed plans to sell its Baton Rouge vinyl chloride complex, including production facilities for 1,2-dichloroethane, to ICI Americas.

[d] Goodrich Chemical Co. has announced plans to construct a 1,2-dichloroethane plant in Convent, Louisiana, that will have an annual capacity of 0.36 million metric tons.

[e] A planned expansion of vinyl [illegible] plant at Lake Charles was announced in July 1978 by PPG Industries, Inc.

Source: US EPA, 1979a



Source: Adapted from ORNL(EPA 1979a)

FIGURE 2.3 PRODUCTION OF EDC VIA THE DIRECT CHLORINATION PROCESS

2.1.1.1 Emission to Air

According to the flow diagram of the direct chlorination process (Figure 2.3), EDC emissions to air can occur at the following sources: (a) the chlorinator vent (Stream A of Figure 2.3), (b) the light-end column vent (Stream B of Figure 2.3), (c) the EDC distillation column vent (Stream C of Figure 2.3), (d) product storage tanks (Stream D of Figure 2.3) and (e) miscellaneous fugitive emissions.

The emission factors of EDC to air from Streams A, B, and C are, respectively, 1.6 kg, 1.7 kg and 1.7 kg, based on 1.6 kg of EDC produced (EPA, 1979a), or 1.0 kg, 1.0 kg and 1.0 kg, based on 1 kkg of EDC produced . The combined emission factor obtained from Bellamy & Schwartz is 3.0 kg/kkg of EDC produced (EPA, 1979a). Comparing this emission factor to that of Hedley et al. (1975), (7.5 kg/kkg), we arrive at a +150% deviation. We also assume that some emission of EDC to air must exist in this process, therefore, the lower bound of the uncertainty of the combined emission factor is estimated at -95%.

a. Emission of EDC to Air From The Chlorinator Vent (Stream A)

A 1.6 kg/1.64 kkg of EDC produced is released uncontrolled to the atmosphere in the direct chlorination process (EPA, 1979a). According to Section 2.1.1.1, we assume that the uncertainty of this emission factor is also +150%, and -95%.

The quantity of EDC emitted uncontrolled to the air from the chlorinator vent can be calculated as follows:

$(2.94 \times 10^{6}$ kkg) $(1.6 \times 10^{-3}$ kkg/1.64 kkg) = 2.9×10^{3} kkg

where;

2.94×10^{6} kkg = quantity of EDC produced by the direct chlorination process

1.6×10^{-3} kkg/1.64 kkg = emission factor obtained from EPA, 1979a

2.9×10^{3} kkg = amount of EDC released uncontrolled to the air from the chlorinator vent

If we assume that the uncertainty of the emission factor is +150% and -95%, and that of the production figure is ± 1%, then the uncertainty of the uncontrolled emission quantity is +150% and -96%.

The information on the method of emission control of this source does not exist in the literature.

Assuming that this emission source is equipped with an incinerator (typical in many processes) which serves as an emission control device, and also assuming that a 98% control efficiency can be achieved, then the controlled emission from the chlorinator vent can be calculated as follows:

$(2.9 \times 10^3 \text{ kkg})\ (0.02) = 58 \text{ kkg}$

where;

2.9×10^3 kkg = the uncontrolled emission quantity

0.02 = the inefficiency factor of the incinerator

58 kkg = the controlled emission quantity from the chlorinator vent

The uncertainty of this figure is +530% and -100% because of the following factors: (a) the uncontrolled emission quantity has an uncertainty of +150%, and -96%, and (b) the typical observed range of the destruction efficiency of an incinerator is from 95% to 100%, or the inefficiency factor range of 0% to 5% (or +150% and -100%).

b. Emission of EDC to Air From The Light-End Column (Vent B)

The estimated emission factor of EDC to air from this source is 1.7 kkg/1.64 kkg of EDC produced (EPA, 1979a). The uncertainty of this figure is also +150% and -95%, as discussed in Section 2.1.1.1.

The uncontrolled emission of EDC from the light-end column vent can be calculated by multiplying the quantity of EDC produced via the direct chlorination process by the obtained emission factor. In that case,

$(2.94 \times 10^6 \text{ kkg})\ (1.7 \times 10^{-3} \text{ kkg}/1.64 \text{ kkg}) = 3.0 \times 10^3 \text{ kkg}$

The uncertainty of this figure is +150% and -96% because of the uncertainty of the production figure of ± 1% and the uncertainty of the emission factor of +150% and -95%.

Assuming that this emission source is controlled by using a scrubber of 90% removal efficiency (typical scrubber efficiency ranges from 85% to 92%), then the controlled emission of EDC to air from the light-end column vent can be calculated as follows:

$$(3.0 \times 10^3 \text{ kkg})\ (0.1) = 3.0 \times 10^2 \text{ kkg}$$

where:

3.0×10^3 kkg = uncontrolled emission of EDC from Vent B

0.1 = the inefficiency factor of the scrubber

3.0×10^2 kkg = quantity of EDC released from this source

This figure has an uncertainty of +280% and -97% because of the uncertainty of the uncontrolled emission (+150%, and -96%), and the uncertainty of the inefficiency factor of the scrubber (+50% and -20%).

c. Emission of EDC to Air From The EDC Distillation Column Vent (Stream C)

There is no information available on the emission to the air from the EDC distillation column vent. We assume that the emission factor obtained for the light-end column vent (Stream B) can also be used in calculating the emission of EDC from the EDC distillation column vent. In that case, the emission factor of EDC to air from this source is also 1.7 kg/1.64 kkg of EDC produced. The uncertainty of this figure is +200% and -95%, since we expect that more EDC can be emitted from this source because in this column, EDC is drawn out as a head stream.

The uncontrolled quantity of EDC released from the distillation column vent can then be calculated as follows:

$$(2.94 \times 10^{6} \text{ kkg})\ (1.7 \times 10^{-3} \text{ kkg}/1.64 \text{ kkg}) = 3.0 \times 10^{3} \text{ kkg}$$

where:

2.94×10^{6} kkg = quantity of EDC produced via the direct chlorination process

1.7×10^{-3} kkg/1.64 kkg = emission factor of EDC to air

3.0×10^{3} kkg = quantity of EDC released from this source

The uncertainty of this figure is +200% and -96% because of the uncertainty of the production quantity (± 1%) and the uncertainty of the emission factor (+200% and -95%).

Assuming that the emission from this source is also controlled by a scrubber which has a 90% removal efficiency (+2%, -6%), then the controlled emission from this source can be calculated as follows:

$$(3.0 \times 10^{3} \text{ kkg})\ (0.1) = 3.0 \times 10^{2} \text{ kkg}$$

The associated uncertainty of this figure is +350% and -97% because of the uncertainty of the uncontrolled emission quantity (+200%, -96%) and the uncertainty of the inefficiency factor of the scrubber (+50%, -20%).

d. Total Quantity of EDC Released Directly to the Air From Vents A, B and C of Figure 2-3

The total quantity of EDC released directly to the air from Vents A, B and C can be calculated by taking the sum of all uncontrolled emissions from these sources. In that case,

$$(2.9 \times 10^{3} \text{ kkg}) + (3.0 \times 10^{3} \text{ kkg}) + (3.0 \times 10^{3} \text{ kkg}) = 8.9 \times 10^{3} \text{ kkg}$$

The uncertainty of this figure is +170% and -96%.

The total controlled quantity of EDC emitted to the air from these sources can also be calculated as follows:

$(58 \text{ kkg}) + (3.0 \times 10^2 \text{ kkg}) + (3.0 \times 10^2 \text{ kkg}) =$

6.6×10^2 kkg

where:

58 kkg = controlled emission from Vent A (+530%, -100%)

3.0×10^2 kkg = controlled emission from Vent B (+280%, -97%)

3.0×10^2 kkg = controlled emission from Vent C (+350%, -97%)

The calculated uncertainty of the above combined controlled emissions quantity is +330% and -97%.

e. Emission of EDC to Air From Product Storage Tanks (Stream D)

There are two kinds of emission from storage tanks: (a) loss due to tank breathing and (b) working loss or loss due to tank cleaning and tank filling.

According to the AP-42 report (EPA, 1977g), emission factors of EDC to air from "old" fixed roof tanks are 0.012 kg/day-10^3 liters because of breathing loss and 0.28 kg/10^3 liters because of working loss.

(1) Emission of EDC to Air Because of Tank Breathing

Tank breathing losses are defined by the AP-42 report as the losses resulting from the vapor expelled from a tank because of the thermal expansion of existing vapors, vapor expansion as a result of barometric pressure changes, and/or an increase in the amount of vapor because of added vaporization in the absence of a liquid-level change (EPA, 1977g).

To calculate the amount of EDC lost to the air because of tank breathing, we make the following assumptions:

- EDC is stored in fixed roof tanks, and the tank condition is old;
- All EDC produced is stored for at least one day before it is distributed for other uses; and

- There are 360 days in a working year, based on a typical three turnovers per year (for cleaning purposes).

Based on the above assumptions, the annual emission factor because of breathing loss can be calculated by multiplying the daily emission factor by the number of estimated working days in a year. In that case,

$$(0.012 \text{ kg/day-}10^3 \text{ liters})\ (360 \text{ days/year}) = 4.3 \text{ kg/year-}10^3 \text{ liters}$$

The estimated quantity of EDC lost directly to the air because of tank breathing can then be calculated as follows:

$$(4.3 \text{ kg/year-}10^3 \text{ liters})\ (2.94 \times 10^6 \text{ kkg})\ (10^3 \text{ liters}/1.24 \text{ kkg}) =$$

$$1.0 \times 10^7 \text{ kg or } 1.0 \times 10^4 \text{ kkg/year}$$

where:

$4.3 \text{ kg/year-}10^3 \text{ liters}$ = emission factor because of tank breathing

2.94×10^6 kkg = quantity of EDC produced via the direct chlorination process

10^3 liters/1.24 kkg = the reciprocal of EDC density (1.24 kg/1 @20°C)

The uncertainty of this figure is ±50% because of the uncertainty of the production figure (±10%), the uncertainty of the emission factor (±20%), and the uncertainty of the number of fixed roof tanks still in use as EDC storage tanks (±29%).

Assuming that the emission to air due to tank breathing can be controlled by a refrigerated vapor recovery system which has a 95% recovery efficiency (typical range of vapor recovery system is 90% to 98% efficient) EPA, 1979g, we can calculate the <u>controlled emission</u> to air because of tank breathing as follows:

$$(1.0 \times 10^4 \text{ kkg})\ (0.05) = 5.0 \times 10^2 \text{ kkg})$$

where:

1.0×10^4 kkg = uncontrolled emission because of tank breathing

0.05 = the inefficiency factor of the recovery system

5.0×10^2 kkg = quantity of EDC emitted to the air after control

The uncertainty of this figure is +200% and -80% as a result of the following factors: (a) the uncertainty of the uncontrolled emission quantity is ±50%; (b) the uncertainty of the recovery system efficiency is (+3%, -5%), or the uncertainty of the percentage lost through the recovery system of +100% and -60%.

(2) Emission of EDC to Air Because of Working Loss

Emission of EDC resulting from handling and tank filling is called working loss.

According to the AP-42 report (EPA, 1977g), the emission factor of EDC to air because of tank filling and handling is 0.28 kg/10^3 liters. Based on essential knowledge of typical handling and tank filling methods, we can assign an uncertainty value of ±30% to this emission factor.

The estimated quantity of EDC released uncontrolled to the air during tank filling and handling can be calculated by multiplying the volume of EDC produced via the direct chlorination process by the emission factor obtained from the AP-42 report. In that case,

(0.28 kg/10^3 liters of EDC throughput) (2.94×10^6 kkg) (10^3 liters/1.24 kkg) = 6.0×10^2 kkg

where:

2.94×10^6 kkg = production of EDC via the direct chlorination process

0.28 kg/10^3 liters throughput = emission factor obtained from AP-42

10^3 liters/1.24 kkg = the reciprocal of the EDC density

The uncertainty of this figure is ±31%, based on a ±30% uncertainty of the emission factor and a ±1% uncertainty of the production quantity.

Assuming that the emission from this source can also be controlled by installing a refrigerated vapor recovery system in the source, and also assuming that the recovery system has a 95% (+3%, -5%) efficiency (See Section 2.1.1.1, paragraph e (1)), then the controlled emission of EDC from this source can be calculated as follows:

$$(6.6 \times 10^2 \text{ kkg})\ (0.05) = 33 \text{ kkg}$$

The uncertainty of this figure is +160% and -72%, based on a ±31% uncertainty of the uncontrolled emission quantity and the uncertainty of the percentage lost through the recovery system of +100% and -60%.

f. Emission to Air From Miscellaneous Fugitive Emission Sources

Sources of fugitive emissions within the production plant include process pump, compressors, process valves, and pressure-relief devices. According to Bellamy and Schwartz (EPA, 1979a), these fugitive emissions amount to 0.1 kg/1.64 kkg of produced. We also assign a ±150%, -95% uncertainty to the figure for the same reasons stated in Section 2.1.1.1.

The quantity of EDC emitted to the air because of fugitive emissions can then be calculated by multiplying the quantity produced by the direct chlorination process by the emission factors. Therefore:

$$(2.94 \times 10^6 \text{ kkg})\ (0.1 \text{ kg}/1.64 \text{ kkg}) = 1.8 \times 10^2 \text{ kkg}$$

The uncertainty of this figure ±150%, -96%, results from the uncertainty of the emission factor (+150%, -95%), and a ±1% uncertainty of the production quantity.

Assuming that 90% (±10%) of the fugitive emissions can be controlled by regular maintenance procedure, quick response and repair of leaks, then the controlled emission of EDC from fugitive emission sources can be calculated as follows:

$$(1.8 \times 10^2 \text{ kkg})\ (0.1) = 18 \text{ kkg}$$

The uncertainty of this figure is +340% and -100%, as a result of the uncertainty of the uncontrolled emission (+150%, -96%) and the uncertainty of the uncontrolled percentage (+110%, -90%).

2.1.1.2 Emission to Water (Stream E)

We assume that the same percentage of the total emission from the direct chlorination process given by the ORNL report (EPA, 1979a) can also be applied in this report. According to the ORNL report, the percentages of emission to air, land and water are, respectively, 57%, 14%, and 29%.

The waterborne emission factor can then be calculated by multiplying the air emission factor by the ratio of 29% to 57%. In that case,

$$(3.0 \text{ kg/kkg}) \ (29\%/57\%) = 1.5 \text{ kg/kkg}$$

Then, the uncontrolled waterborne emission discharged by the direct chlorination process can be calculated as follows:

$$(2.94 \times 10^6 \text{ kkg}) \ (1.5 \text{ kg/kkg}) = 4.4 \times 10^3 \text{ kkg}$$

The uncertainty of this figure, +150% and -96%, results from the uncertainty of the production quantity (±1%) and the uncertainty of the emission factor (+150%, -95%).

a. Emission to Air Because of Wastewater Treatment

Due to the high volatility of EDC, we assume that 100% of EDC discharged by the production process to water is re-released to the air from the wastewater treatment system (particularly during the secondary treatment phase, which consists of aerated sludge treatment process). Therefore, the quantity of EDC re-released to the air because of the wastewater treatment is 4.4×10^3 kkg, +150%, -96%.

2.1.1.3 Emission to Land (Stream F)

As it was suggested by Bellamy and Schwartz (EPA, 1979a), the quantity of EDC released to land as heavy-end waste is estimated at 1.2 kg/1.64 kkg of product. The uncertainty of this figure is also +150%, -95% (for the same reason stated in Section 2.1.1.1).

The uncontrolled emission of EDC to land as heavy-end waste can then be calculated by multiplying the quantity of EDC by the direct chlorination process by the emission factor. Therefore,

$$(2.94 \times 10^6 \text{ kkg}) \ (1.2 \text{ kg/1.64 kkg}) = 2.2 \times 10^3 \text{ kkg}$$

The uncertainty of this figure is +150%, -96% because of a ±1% uncertainty of the production figure and +150%, -95% uncertainty of the emission factor.

a. Emission of Air Because of Incineration of Heavy-End Waste

Most of the EDC production plants incinerate their heavy-end waste. The typical efficiency of the incinerator is 95%, ±2%; therefore, we assume that 5% of the heavy-end waste escapes intact to the air from the incinerator. The uncertainty of this percentage is ±38%.

The quantity of EDC released to the air as a result of the incineration of solid waste can be calculated by multiplying the quantity of EDC discharged as solid waste by 5%. Then,

$$(2.2 \times 10^3 \text{ kkg})\ (0.05) = 1.1 \times 10^2 \text{ kkg}$$

The uncertainty of this figure is +250%, -98% because of the uncertainty of the uncontrolled heavy-end waste (+150%, and -96%) and the uncertainty of the undestroyed percentage (±38%).

b. Emission to Land Because of Incineration of Heavy-End Waste

We assume that the amount of EDC remaining in the ash after the incineration of heavy-end wastes is negligible.

2.1.1.4 Multimedia Environmental Losses

Figure 2.4 shows environmental losses of EDC from the direct chlorination production process.

2.1.2 Releases of EDC Associated With the Oxychlorination Process

The remainder of the EDC manufactured industrially, 2.05 million kkg in 1977 (EPA, 1979a), was produced by the oxychlorination of ethylene with hydrogen chloride and oxygen in the presence of a catalyst (probably $CuCl_2$). All EDC produced via this process is an intermediate in the production of vinyl chloride monomer (SRI, 1975, EPA, 1978a). The main

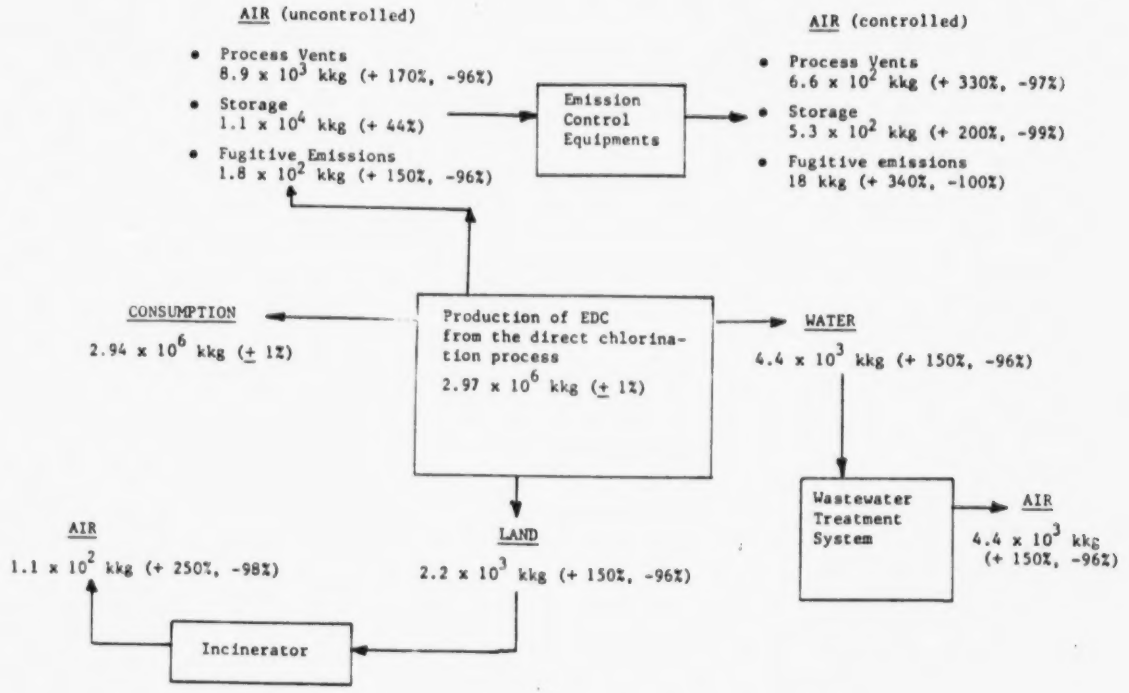

AIR (uncontrolled)
• Process Vents
8.9 x 10^3 kkg (+ 170%, -96%)
• Storage
1.1 x 10^4 kkg (+ 44%)
• Fugitive Emissions
1.8 x 10^2 kkg (+ 150%, -96%)
Emission Control Equipments
AIR (controlled)
• Process Vents
6.6 x 10^2 kkg (+ 330%, -97%)
• Storage
5.3 x 10^2 kkg (+ 200%, -99%)
• Fugitive emissions
18 kkg (+ 340%, -100%)
CONSUMPTION
2.94 x 10^6 kkg (± 1%)
Production of EDC from the direct chlorination process
2.97 x 10^6 kkg (± 1%)
WATER
4.4 x 10^3 kkg (+ 150%, -96%)
Wastewater Treatment System
AIR
4.4 x 10^3 kkg (+ 150%, -96%)
AIR
1.1 x 10^2 kkg (+ 250%, -98%)
LAND
2.2 x 10^3 kkg (+ 150%, -96%)
Incinerator

FIGURE 2.4 ENVIRONMENTAL RELEASES OF EDC FROM THE DIRECT CHLORINATION PROCESS

reaction involved in this process is as follows:

$$CH_2 = CH_2 + 2HCl + \tfrac{1}{2}O_2 \xrightarrow{\text{Catalyst}} ClCH_2CH_2Cl + H_2O$$

A detailed description of this production process is given in Appendix B. Figure 2.5 is a simplified flow diagram of the oxychlorination process.

2.1.2.1 Emission to Air

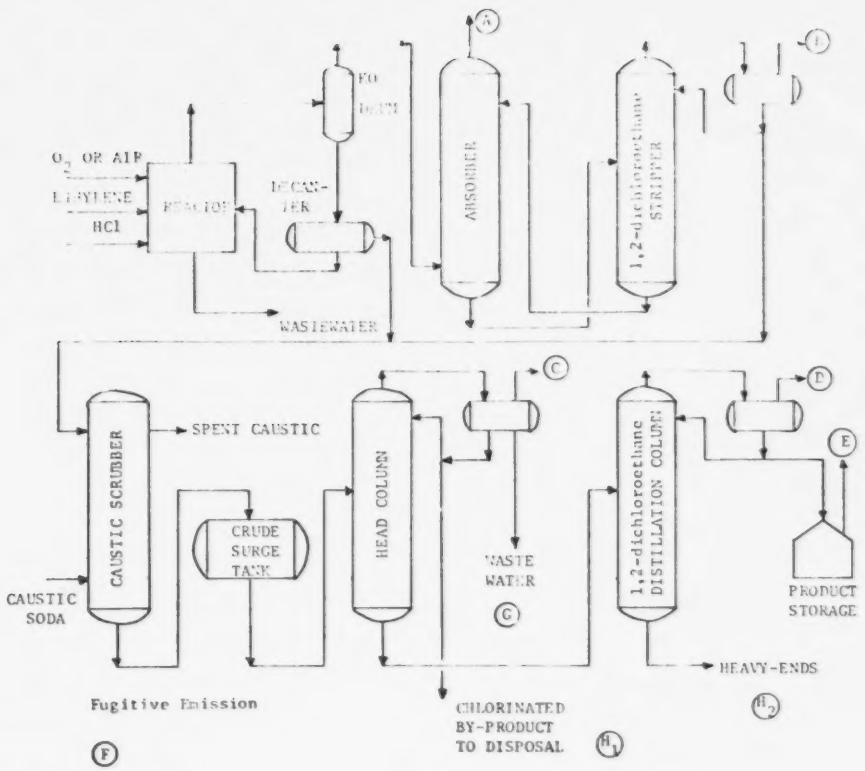
According to the flow diagram of the oxychlorination process (Figure 2·5), EDC emissions to air can occur at the following sources: (a) the absorber vent (Stream A), (b) the EDC stripper vent (Stream B), (c) the light-end column vent (Stream C), (d) the EDC distillation column vent (Stream D), (e) product storage tanks (Stream E), and (f) miscellaneous fugitive emissions. The obtained emission factors of Streams A, B, C, and D are, respectively, 1.7 kg, 4.5 kg, 1.7 kg and 1.7 kg, based on 1.64 kkg of EDC produced (EPA, 1979a). The combined emission factor of these sources amounts to 9.6 kg/1.64 kkg of EDC produced (or 5.9 kg/kkg). Comparing this emission factor to that of ORNL (EPA, 1979a) (11.4 kg/kkg), we arrive at a +93% upper-bound deviation. We also expect that some emission of EDC to air must exist in the oxychlorination process; therefore, the lower bound of the uncertainty of the emission factor must be greater than -100%. Thus for the simplicity of the calculation, we assume that an uncertainty of ±95% can be assigned to the combined emission factor.

a. Emission of EDC to Air from the Absorber Vent (Stream A)

According to Bellamy and Schwartz (1975), a 1.7 kg/kkg of EDC produced is released uncontrolled to the air in the oxychlorination process (EPA, 1979a). As it is stated in the above section, the same bounds of uncertainty can also be assigned to this emission factor (±95%).

The uncontrolled quantity of EDC emitted to the air can be calculated as follows:

$$(2.05 \times 10^6 \text{ kkg})\ (1.7 \times 10^{-3} \text{ kkg}/1.64 \text{ kkg}) = 2.1 \times 10^3 \text{ kkg}$$



Source: Adapted from ORNL (USEPA, 1979a)

FIGURE 2.5 PRODUCTION OF EDC VIA THE OXYCHLORINATION PROCESS

Where:

2.05×10^6 kkg = quantity of EDC produced by the oxychlorination process

1.7 kg/1.64 kkg = emission factor obtained from EPA, 1979a.

2.1×10^3 kkg = uncontrolled emission of EDC from the absorber vent

The uncertainty of this figure is estimated at ±96%, based on the uncertainty of the production quantity (±1%) and the uncertainty of the emission factor (±95%).

Assuming that this emission source is controlled by a scrubber of 90% efficiency (+2%, -6%) (see Section 2.1.1.1.b,c), then the controlled emission from the absorber vent can be calculated by multiplying the uncontrolled emission quantity by the percentage of gas escaped intact from the scrubber.

Therefore:

$$(2.1 \times 10^3 \text{ kkg}) (0.1) = 2.1 \times 10^2 \text{ kkg}$$

The uncertainty of this figure is +190% and -97% because of the uncertainty of the uncontrolled emission quantity (±96%) and the uncertainty of the inefficiency factor of the scrubber (+50%, -20%).

b. Emission of EDC to Air from the EDC Stripper Vent (Stream B)

The estimated uncontrolled emission factor is 4.5 kg/1.64 kkg of EDC produced (EPA, 1979a). The uncertainty of this figure is also ±95% (see Section 2.1.2.1).

The uncontrolled emission of EDC from the EDC stripper vent can be calculated as follows:

$$(2.05 \times 10^6 \text{ kkg}) (4.5 \times 10^{-3} \text{ kkg}/1.64 \text{ kkg}) = 5.6 \times 10^3 \text{ kkg}$$

where:

2.05×10^6 kkg = quantity of EDC produced via the oxychlorination process

4.5×10^{-3} kkg/1.64 kkg = emission factor obtained from (EPA, 1979a)

and,

5.6×10^3 kkg = quantity of EDC released uncontrolled to the air from the EDC stripper vent

The uncertainty of this figure is ±96% because of a ±1% uncertainty of the production figure and a ±95% uncertainty of the emission factor.

We also assume that there is an incinerator of 98% (+2%, -4%) efficiency used as emission control equipment on this source; then the controlled emission of EDC to air from the EDC stripper vent can be calculated by multiplying the uncontrolled emission quantity by the inefficiency factor of the incinerator. In that case,

$$(5.6 \times 10^3 \text{ kkg}) (0.02) = 1.1 \times 10^2 \text{ kkg}$$

The uncertainty of this figure is calculated at +500%, and -100%, based on the following factors: (a) the uncertainty of the uncontrolled emission quantity is ±96%, (b) the uncertainty of the inefficiency factor of the incinerator is +200% and -100%.

c. Emission of EDC to Air from the Light-End Column Vent (Stream C)

There is no information available on the emission of EDC to the air from the light-end column vent. Assuming that the emission factor obtained from the light-end column vent of the direct chlorination process can also be applied for this process, then the emission factor of EDC to air from this source is estimated at 1.7 kg/1.64 kkg of EDC produced (see Section 2.1.1.1, paragraph b). The assigned uncertainty value of this figure is also ±95% (see Section 2.1.2.1 for reasons).

The uncontrolled emission of EDC from the light-end column can be estimated by multiplying the quantity of EDC produced via the oxychlori-

nation process by the emission factor obtained. Therefore,

$$(2.05 \times 10^3 \text{ kkg}) (1.7 \times 10^{-3} \text{ kkg}/1.64 \text{ kkg}) = 2.1 \times 10^3 \text{ kkg}$$

The uncertainty of this figure is 96%. The rationale for this uncertainty is the same as stated in Section 2.1.2.1, paragraph a.

Assuming that there exists an emission control device on this source such as a scrubber of 90% (+2%, -6%) efficiency, then the controlled emission from this source can be calculated as follows:

$$(2.1 \times 10^3 \text{ kkg}) (0.1) = 2.1 \times 10^2 \text{ kkg}$$

where:

2.1×10^3 kkg = uncontrolled emission of EDC to air from the light-end column vent

0.1 = the inefficiency factor of the scrubber

2.1×10^2 kkg = quantity of EDC released after control from this source

The uncertainty of this figure is also +190%, and -97% because of the uncertainty of the uncontrolled emission quantity (±96%) and the uncertainty of the inefficiency factor of the scrubber (+50%, -20%).

d. Emission of EDC to Air from the EDC Distillation Column Vent (Stream D)

The information on the emission of EDC from this source does not exist in the literature. We assume that the emission factor obtained for the EDC distillation column vent in the direct chlorination process is also applicable for the oxychlorination process; thus the estimated emission factor from this source is 1.7 kg/1.64 kkg (See Section 2.1.1.1, paragraph c). The uncertainty of this figure is also ±95%.

The uncontrolled emission of EDC to the air from the EDC distillation column vent can then be calculated by multiplying the quantity of EDC produced by the oxychlorination process by the emission factor. Therefore:

$$(2.05 \times 10^6 \text{ kkg}) (1.7 \times 10^{-3} \text{ kkg}/1.64 \text{ kkg}) = 2.1 \times 10^3 \text{ kkg}$$

The uncertainty of this figure is ±95%. This value was obtained based on an uncertainty of ±1% of the production quantity and an uncertainty of ±95% of the emission factor.

We also assume that this emission source is controlled by a scrubber of 90% (+2% and -6%) efficiency; then the controlled emission from this source can be calculated as follows:

$$(2.1 \times 10^3 \text{ kkg})\ (0.1) = 2.1 \times 10^2 \text{ kkg}$$

where:

2.1×10^3 kkg = uncontrolled emission of EDC to air

0.1 = the inefficiency factor of the scrubber

2.1×10^2 kkg = quantity of EDC released after control from this source

The uncertainty of this figure is also +190% and -97% (see reasons in Section 2.1.2.1, paragraph e).

e. Total Emission of EDC to Air from Streams A, B, C and D of Figure 2.5

The total uncontrolled quantity of EDC emitted to the air from Streams A, B, C and D can be calculated by taking the sum of the emissions from these streams. Therefore:

$$(2.1 \times 10^3 \text{ kkg})_4 + (5.6 \times 10^3 \text{ kkg}) + (2.1 \times 10^3 \text{ kkg}) + (2.1 \times 10^3 \text{ kkg}) = 1.2 \times 10^4 \text{ kkg}$$

The uncertainty of this figure is ±96%.

The total controlled quantity of EDC released to the air from these sources can also be calculated as follows:

$$(2.1 \times 10^2 \text{ kkg})_2 + (1.1 \times 10^2 \text{ kkg}) + (2.1 \times 10^2 \text{ kkg}) + (2.1 \times 10^2 \text{ kkg}) = 7.4 \times 10^2 \text{ kkg}$$

where:

2.1×10^2 kkg = the controlled emission of EDC to air from Stream A (+190%, -97%)

1.1×10^2 kkg = the controlled emission of EDC to air from Stream B (+500%, -100%)

2.1×10^2 kkg = the controlled emission of EDC to air from Stream C (+190%, -97%)

2.1×10^2 kkg = the controlled emission of EDC to air from Stream D (+190%, -97%)

The resulting uncertainty of the combined control quantity is +240% and -97%.

f. Emission of EDC to Air from Product Storage Tanks

As is pointed out in Section 2.1.1.1, paragraph e, there are two kinds of loss from product storage tanks: (a) tank breathing loss and (b) working loss.

We assume that the same emission factors obtained in Section 2.1.1.1, paragraph e are applicable to the calculation of EDC emission from storage tanks in this process: (a) 0.012 kg/day-10^3 liters or 4.3 kg/year-10^3 liters for tank breathing loss, and (b) 0.28 kg/10^3 liters for working loss (EPA, 1977g).

(1) Emission of EDC to Air from Tank Breathing Loss

The quantity of EDC released uncontrolled as a result of breathing loss can be calculated by multiplying the quantity of EDC produced by the oxychlorination process by the emission factor.

In that case,

$(2.05 \times 10^6$ kkg) $(4.3 \times 10^{-3}$ kkg/yr-10^3 liters) (10^3 liters/1.24 kkg)
$= 7.1 \times 10^3$ kkg

where:

2.05×10^6 kkg = quantity of EDC produced via the oxychlorination process

4.3×10^{-3} kkg/yr-10^3 liters = emission factor

10^3 liters/1.24 kkg = the reciprocal of EDC density (1.24 kg/1 @20°C)

7.1×10^3 kkg = quantity of EDC released uncontrolled to the air from this source

The uncertainty of this figure is ±50% because of the following factors: (a) the uncertainty of the production figure is 1%; (b) the uncertainty of the emission factor is ±20%; and (c) the uncertainty of the number of fixed roof tanks still in use by the industry is ±29%.

Assuming that the emission to air because of tank breathing can be controlled by a refrigerated vapor recovery system which has a 95% (+3%, -5%) recovery efficiency (EPA, 1977g), the controlled emission can then be calculated as follows:

$$(7.1 \times 10^3 \text{ kkg})\ (0.05) = 3.6 \times 10^2 \text{ kkg}$$

where:

7.1×10^3 kkg = uncontrolled EDC emission because of tank breathing

0.05 = the inefficiency factor of the vapor recovery system

3.6×10^2 kkg = quantity of EDC released after control

The uncertainty of this figure is +200% and -80% [see Section 2.1.1.1, paragraph e (1)].

(2) Emission of EDC to Air Because of Working Loss

According to Section 2.1.2.1, paragraph f, the emission factor because of working loss is 0.28 kg/10^3 liters. Using this emission factor, we can then calculate the release of EDC to the air as a result of tank filling. In this case:

$$(2.05 \times 10^6 \text{ kkg}) (0.28 \text{ kg}/10^3 \text{ liters}) (10^3 \text{ liters}/1.24 \text{ kkg}) = 4.6 \times 10^2 \text{ kkg}$$

The uncertainty of this figure is ±31% because of the uncertainty of the emission factor (±30%) [see Section 2.1.1.1, paragraph e (2)] and the uncertainty of the production quantity (±1%).

We also assume that the emission from this source can be controlled by a vapor recovery system of 95% efficiency (+3%, -5%) [see Section 2.1.1.1, paragraph e (1)]; then the controlled emission of EDC to the air from this source can be calculated as follows:

$$(4.6 \times 10^2 \text{ kkg}) (0.05) = 2.3 \text{ kkg}$$

The uncertainty of this figure is also +160% and -72% [see Section 2.1.1.1, paragraph e (2)].

g. Emission of EDC to Air from Miscellaneous Sources

As is mentioned in Section 2.1.1.1, paragraph f, the emission factor of EDC to air from fugitive emission sources is 0.1 kg/1.64 kkg of EDC produced (see Section 2.1.1.1, paragraph f). The uncontrolled emission of EDC to air from these miscellaneous sources can then be calculated as follows:

$$(2.05 \times 10^6 \text{ kkg}) (0.1 \text{ kg}/1.64 \text{ kkg}) = 1.3 \times 10^2 \text{ kkg}$$

The uncertainty of this figure is ±96% because of the following factors: (a) the uncertainty of the production quantity is ±1%; (b) the uncertainty of the emission factor is ±95% (see Section 2.1.2.1).

Assuming that 90% (±10%) of the fugitive emissions can be controlled by proper maintenance procedures, then the controlled emission from these sources can be calculated as follows:

$$(1.3 \times 10^2 \text{ kkg})\ (0.1) = 13 \text{ kkg}$$

where:

1.3×10^2 kkg = the uncontrolled emission of EDC from fugutive sources

0.1 = the inefficiency factor

13 kkg = the controlled emission of EDC from this source

The uncertainty of this figure is +310% and -100% because of the uncertainty of the uncontrolled emission (±96%) and the uncertainty of the inefficiency factor (+110%, -90%).

2.1.2.2 Emission to Water (Stream G)

The information on the quantity of EDC emitted from this stream does not exist in the Hedley report (Hedley et al., 1975); therefore, by assuming the same percentage of the total emission from the oxychlorination process given by ORNL (EPA, 1979a), the emission factor of EDC to water can be calculated as follows:

[5.9 kg/kkg (to air)] [24.5% (to water/61% (to air)] = 2.4 kg/kkg

where:

5.9 kg/kkg = emission factor to air obtained in this report (see Section 2.1.2.1)

24.5%/61% = the ratio of the percentage of the total emission to water and the percentage of the total emission to air (EPA, 1979a)

2.4 kg/kkg = emission factor to water

The uncontrolled emission of EDC to water can be calculated by multiplying the quantity of EDC produced via the oxychlorination process by

the emission factor. In that case,

$$(2.05 \times 10^6 \text{ kkg})\ (2.4 \text{ kg/kkg}) = 4.9 \times 10^3 \text{ kkg}$$

The uncertainty of this figure is ±96% because of the uncertainty of the production quantity (±1%) and the uncertainty of the emission factor (±95%).

a. Emissions to Air Because of Wastewater Treatment

As is mentioned in Section 2.1.1.2, paragraph a, the quantity of EDC emitted to water is all re-released to the air as a result of evaporation from the aerated sludge treatment system. Thus we assume that this quantity amounts to 4.9×10^3 kkg, ±96%.

2.1.2.3 Emissions to Land

According to Figure 2.5, emissions of EDC to land can occur in the following sources: (a) the heavy-end waste stream from the light-end column (Stream H of Figure 2.5), and (b) the heavy-end waste stream from the EDC distillation column (Stream I of Figure 2.5).

According to Bellamy & Schwartz (1975), the emission factor of EDC released in the heavy-end waste stream from the EDC distillation column (Stream I) is estimated at 1.2 kg/1.64 kkg of EDC produced (or 0.73 kg/kkg of EDC) (EPA, 1979a). There is no information on the emission factor of EDC released in Stream H. We then assume that the emission factor from Stream H is also 1.2 kg/1.64 kkg of EDC. This assumption should be verified in later studies. The combined emission factor to land resulting from these two sources can be calculated by taking the sum of the two emission factors. Therefore:

$$(1.2 \text{ kg/1.64 kkg})\ (2) = 2.4 \text{ kg/1.64 kkg or } 1.5 \text{ kg/kkg}$$

Comparing this figure to that of ORNL (EPA, 1979a) (2.75 kg/kkg), we arrive at a +83% deviation. Assuming that the lower bound of uncertainty is -95% because some emissions of EDC must exist in these sources, then the uncertainty of the combined emission factor is +83%, and -95%.

Based on the above assumptions, the total quantity of EDC emitted directly to land in heavy-end waste streams can be calculated by multiplying the quantity of EDC produced via the oxychlorination process by the combined emission factor. In that case:

$$(2.05 \times 10^6 \text{ kkg}) (1.5 \text{ kg/kkg}) = 3.1 \times 10^3 \text{ kkg}$$

The uncertainty of this uncontrolled emission quantity is +84%, -96%, as a result of the following factors: (a) the uncertainty of the emission factor is +83% and -95%; and (b) the uncertainty of the production quantity is ±1%.

a. Emission to Air Because of Incineration of Heavy-End Waste Streams

We assume that all heavy-end wastes discharged by the industry are incinerated, and that the incinerator can achieve a 95% destruction efficiency (incinerator efficiency typically ranges from 93% to 97%); therefore, 5% of the heavy-end wastes can escape intact to the air. The uncertainty of the inefficiency factor of the incinerator is estimated at ±38%.

The quantity of EDC released uncontrolled to the air from incineration of heavy-end wastes can then be calculated as follows:

$$(3.1 \times 10^3 \text{ kkg}) (0.05) = 1.6 \times 10^2 \text{ kkg}$$

where:

3.1×10^3 kkg = quantity of EDC discharged in heavy-end wastes

0.05 = the inefficiency factor of the incinerator

1.6×10^2 kkg = the quantity of EDC released to air after control

The uncertainty of this figure is +150%, -98%, because of a ±38% uncertainty of the inefficiency factor of the incinerator and a +84% and -96% uncertainty of the quantity of EDC present in heavy-end wastes.

b. Emission to Land After Incineration of Heavy-End Waste

We assume that the amount of EDC remaining in the ash after the incineration phase is negligible.

2.1.2.4 Multimedia Environmental Losses

Figure 2.6 shows environmental losses of EDC in the oxychlorination process.

2.2 ENVIRONMENTAL RELEASES OF EDC ASSOCIATED WITH INDIRECT PRODUCTION PROCESSES

Indirect sources of EDC production include all other production of EDC, even that which occurs inadvertently. There was no indication in the literature that any natural sources of EDC exist. The sources identified are:

- chlorination of public water supplies
- chlorination of wastewater
- incineration of chlorinated organics
- other industrial manufacturing processes
- laboratory preparations
- releases from stockpiles

2.2.1 Releases of EDC Associated With the Chlorination of Public Water Supplies

In the chlorination of water at water treatment facilities, small quantities of EDC are found to be produced. It is hypothesized the chlorine reacts with organic impurities in the water to produce EDC (Symons et al., 1975). In 1975 and 1976, the USEPA conducted the National Organics Reconnaissance Survey (NORS) and the National Organic Monitoring Survey (NOMS) to examine raw and finished water samples for the presence of halogenated organic compounds in drinking water. The results of NORS indicated that EDC was not found in high concentrations, or even frequently, in public water supplies. The highest concentration in raw water was 3 μg/liter, while that in finished water was 6 μg/liter.

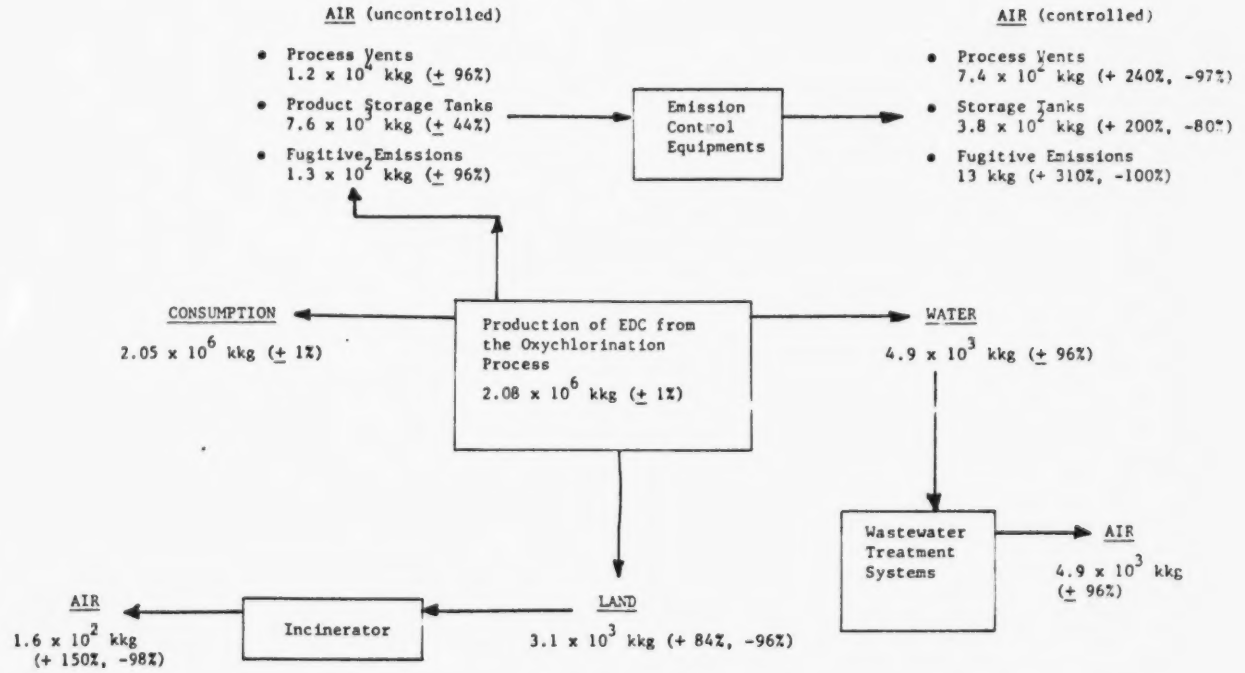


FIGURE 2.6 ENVIRONMENTAL RELEASES OF EDC FROM THE OXYCHLORINATION PROCESS

(Symons et al., 1975). The NOMS survey indicated that a median value of 2 μg/liter was found in the potable water supplies (Mello, 1978).

To calculate the quantity of EDC produced as a result of the chlorination of water, we make the following assumptions:

- Quantity in finished water minus quantity in raw water equals the quantity of EDC as a result of the chlorination of public water supplies
- U.S. population in 1977 approximated 225×10^6 persons (±5%)
- Water use is on the average of 100 gal./person/day in U.S. (±20%) (Hammer, 1975).

Applying all the assumptions, an estimate of the quantity of EDC in chlorinated public water supplies can be made. First, the total water use per year is calculated by multiplying the total persons by the total gallons used per day per person by total days per year:

$$(225 \times 10^6 \text{ persons}) \times (100 \text{ gal./person/day}) \times (365 \text{ days/year})$$
$$= 8.2 \times 10^{12} \text{ gal./year}$$

The uncertainty of this figure is ±25%, based on the following factors: (a) the uncertainty of the U.S. population is ±5%, and (b) the uncertainty of the daily water use per capita is ±20%.

As presented in Table C.1 of Appendix C, the difference between the quantity of EDC in raw water and that in finished water averages to 0.07 μg/liter (±100%). Using this concentration, we can then calculate the average quantity of EDC produced as a result of chlorination of public water supplies by multiplying this concentration by the total quantity of water used per year:

$$(0.07 \text{ μg/liter}) (8.2 \times 10^{12} \text{ gal./year}) (3.781 \text{ liter/gal.})$$
$$= 2.2 \times 10^{12} \text{ μg/year or 2.2 kkg/year}$$

The uncertainty of this figure is +150% and -100% because of the uncertainty of the obtained concentration (±100%) and the uncertainty of the total quantity of water used per year (±25%).

2.2.2 Releases of EDC Associated With the Chlorination of Industrial Wastewaters

Documentation of the inadvertent production of EDC as a result of the chlorination of wastewater was not found. However, since EDC is produced in the chlorination of public water supplies, it is reasonable to assume that EDC is also produced as chlorine reacts with the organic constituents of wastewater during the chlorination of industrial wastewater. The following assumptions must be made before calculation of the production of EDC:

- Industrial wastewater discharge is (average) twice the amount of water used per capita per year (Hammer, 1975)
- Residential water use in 1977 is estimated at 8.2×10^{12} gal./year (±25%) (see Section 2.2.1)
- The highest concentration found in the NORS survey (3 µg/1) is the typical concentration of EDC formed after the chlorination of industrial wastewater (since industrial wastewater probably contains a higher quantity of substrates than the municipal water supplies).

The quantity of EDC released to the water as a result of the chlorination of wastewater can be calculated by multiplying the concentration of EDC produced in wastewater by the total amount of chlorinated wastewater in the U.S.

$$(3\ \mu g/1) \times (kkg/10^{12}\ \mu g) \times (8.2 \times 10^{12}\ \text{gal./year} \times (2) \times (3.781\ 1/\text{gal.})$$
$$= 1.9 \times 10^{2}\ kkg/year$$

The uncertainty of this figure is +150% and -100% due to the following factors: (a) the uncertainty of industrial water use is ±25% and (b) the uncertainty of the concentration of EDC formed as a result of chlorination of industrial wastewater is ±100%.

2.2.3 Releases of EDC Associated With the Incineration of Chlorinated Organics

EDC gas may be formed during the incineration of chlorinated organics (Derby and Freedman, 1974). The EDC may be present as a contaminant in the material or may be "manufactured" upon incineration. To estimate the quantity of EDC released during incineration, we make the following

assumptions and conditions:

- Chlorinated organics may be incinerated as wastes at industrial facilities
- Production of chlorinated organic compounds in 1977 was 1.03×10^7 kkg (USITC, 1978)
- 0.5% of production (as wastes) are incinerated
- 1.5 ppm of that quantity incinerated is released as EDC.

Therefore, the amount of EDC released is calculated by multiplying the total quantity of chlorinated organic compounds produced in 1977 (1.03×10^7 kkg) by the percentage incinerated (0.5%) and by the concentration of EDC in the off-gases (1-5 ppm).

At 1 ppm:

$$(1.03 \times 10^7 \text{ kkg chlorinated organics}) \times (0.005) \times (1 \text{ kkg EDC}/10^6 \text{ kkg chlorinated organics}) = 0.05 \text{ kkg EDC}$$

At 5 ppm:

$$(1.03 \times 10^7 \text{ kkg chlorinated organics}) \times (0.005) \times (5 \text{ kkg EDC}/10^6 \text{ kkg chlorinated organics}) = 0.3 \text{ kkg EDC}$$

In addition, chlorinated organics may be incinerated as a component of municipal solid wastes. To estimate this quantity, we make the following assumptions and conditions:

- Approximately 120 million kkg of municipal solid waste (MSW) is produced annually in the U.S. (U.S. EPA, 1977f). (±10%)
- Approximately 1% of the total quantity of MSW is incinerated (±20%)
- Approximately 5% of the MSW is chlorinated organic waste (including plastics)
- 1-5 ppm of the chlorinated organic waste incinerated is released as EDC (EPA, 1977f) (±40%).

Therefore, by multiplying the total quantity of MSW (120×10^6 kkg) by the percentage incinerated (1%), by the component, which is chlorinated organics (5%), and by the concentration of EDC in the off-gases (1-5 ppm), the amount of EDC released is calculated.

At 1 ppm:

$$(120 \times 10^6 \text{ kkg MSW}) \times (0.01) \times (0.05) \times (1 \text{ kkg EDC}/10^6 \text{ kkg MSW}) = 0.06 \text{ kkg EDC}$$

At 5 ppm:

$$(120 \times 10^6 \text{ kkg MSW}) \times (0.01) \times (0.05) \times (5 \text{ kkg EDC}/10^6 \text{ kkg MSW}) = 0.3 \text{ kkg EDC}$$

Adding the amount of EDC released from industrial incineration to the EDC released from the incineration, the total EDC released was between 0.1 kkg and 0.6 kkg in 1977.

The above figures have the uncertainty of ±70% because of the following factors: (a) the uncertainty of the quantity of chlorinated organics in MSW is ±40%, (b) the uncertainty of the amount of MSW incinerated per year is ±20%, and (c) the uncertainty of the quantity of MSW released per year is ±10%.

2.2.4 Other Possible Inadvertent Sources of EDC

Possible pathways for indirect production of EDC include biological degradation, photochemical degradation and miscellaneous chemical reactions in rivers, soils, landfills, and the atmosphere.

The most likely source of EDC formation would be the conversion of a number of EDC-related chemicals in the atmosphere. These chemicals would include perchloroethylene, trichloroethylene, vinylidene chloride, methyl chloroform, and vinyl chloride. A variety of reaction mechanisms such as photo-oxidation, ozone attack, hydroxyl substitution and irradiation could produce EDC from the compounds.

Other reactions in the atmosphere that may form EDC include chlorination of ethane; however, chloride radicals in the atmosphere are so rare that negligible quantities of EDC would be expected to form.

Vinylidene chloride ($CH_2 = CCl_2$) emissions to the atmosphere during manufacture or subsequent polymerization are reported to react under certain conditions to form peroxide and epoxide compounds which tend to decompose spontaneously to form HCl, phosgene, various oxygenated organic chlorides and EDC (USEPA, 1977c). It is estimated in this report that total EDC emissions in 1977 from all sources amounted to approximately 600 kkg, all of which entered the atmosphere. Assuming a maximum concentration of atmospheric EDC reconversion at 1 ppm, indirect EDC production from EDC emissions in 1977 is calculated:

$$(1 \text{ ppm EDC}) \times (.99) \times (600 \text{ kkg EDC}) = 5 \times 10^{-4} \text{ kkg}$$

The uncertainty of this figure is +200% and -100% because of the very low possibility of occurrence of this kind of reaction.

EDC formation by biological degradation of EDC precursors is also estimated to be slight. This is a result of the high volatility of these EDC precursors.

2.2.5 Releases of EDC Associated With Other Manufacturing Processes

Another source of EDC release is chemical reactions which do not involve EDC as a starting material or an end product but which can produce EDC as a by-product. A list of possible reactions which can form EDC is presented below:

- Chlorination of methane to form CCl_4 (carbon tetrachloride)
- Chlorination of ethane to form CCl_4 (carbon tetrachloride)
- Chlorination of ethylene to form CH_3CH_2Cl (ethyl chloride) in the presence of Cu, Fe, Sb and Ca chlorides
- Chlorination of ethanol to form CH_3CH_2Cl (ethyl chloride)
- Chlorination of methane to produce methylene chloride (CH_2Cl_2)
- Chlorination of acetylene in the production of perchloroethylene
- Chlorination of acetylene in the production of trichloroethylene
- Chlorination of 1,1-dichloroethane to produce 1,1,1-trichloroethane
- Catalytic addition of HCl to 1,1-dichloroethylene to produce 1,1,1-trichloroethane
- Chlorohydrin processes

- Production of allyl chlorides from propene and Cl_2
- Production of acid chlorides, especially chloroacetyl chloride from carboxylic acids and thionyl chloride
- Chlorination of 1,2-dibromopropane to yield 1,2-dibromochloropropane.

It can be estimated using USITC data that a total of 1.5 million kkg of these other chemicals are produced in the United States. Table 2.2 presents the production data for these chemicals that are related to the production of EDC as a by-product.

The yield of EDC in the above reactions is expected to be very small; a crude estimate would quantify EDC by-product production between 0.5 and 100 ppm (Dow, 1979). Based on these estimates of yield and production figures, the estimated values for the total amount of EDC released as a by-product is shown in Table 2.2.

2.2.6 Releases of EDC Associated With Laboratory Use

In industrial research laboratories, unidentified quantities of EDC are produced as part of ongoing R&D efforts. In this practice, there is potential for wastewater emissions routed to municipal wastewater treatment facilities and air emissions from laboratory hood vents. This is an area for which no data currently exists.

2.3 STOCKPILES

The quantity of EDC that is stockpiled for future use is estimated to be negligible, since there was no data which indicated otherwise. Based upon the available information, no appreciable quantities of EDC are stockpiled for more than three days at a time, whereupon the chemical undergoes further processing. Information on stockpiles of consumer products containing EDC is contained in Section 3.0, Environmental Releases During the Production and Use of Products Made from EDC. Emissions of EDC from stockpiles stored are discussed in Sections 2.1.1 and 2.1.2.

TABLE 2-2

SUMMARY OF RELEASES OF EDC FROM PRODUCTION PROCESSES WHICH DO NOT INVOLVE EDC AS A STARTING MATERIAL OR AN END PRODUCT

CHEMICAL	TOTAL PRODUCTION IN 1977 (KKG)	ESTIMATED QUANTITY PRODUCED[b] WITH EDC AS BY-PRODUCT (KKG)	ESTIMATED RANGE OF EDC RELEASE (KKG) at 0.5 PPM	at 100 PPM
Carbon Tetrachloride	3.7×10^5 [a]	2.8×10^5	0.1	20
Ethyl Chloride	2.8×10^5 [a]	2.8×10^5	0.1	20
Methylene Chloride	2.2×10^5 [a]	2.2×10^5	0.1	20
Perchloroethylene	2.8×10^5 [a]	8.2×10^3	0.004	0.8
Trichloroethylene	1.4×10^5 [a]	13.6×10^3	0.003	0.6
Methyl Chloroform	2.9×10^5 [a]	2.7×10^3	0.001	0.2
Others	1.0×10^4	1.0×10^4	0.005	1.0
TOTAL	1.6×10^6	8.1×10^5	0.3	63

a) Sources: USITC, 1978
b) Based upon knowledge of production processes

2.4 IMPORTS

According to the U.S. Department of Commerce statistics, no EDC has been imported to the United States in the past five years. (U.S. Department of Commerce, 1977).

3.0 ENVIRONMENTAL RELEASES ASSOCIATED WITH THE USE OF EDC

Of the 4.99 million kkg of EDC produced in the United States in 1977, 4.81 million kkg was actually used. The remaining 0.18 million kkg (3%) was exported for use outside the United States (U.S. Department of Commerce, 1977).

The uses of EDC are described in this report in two categories: major uses and minor uses. The major uses account for 99.9% of the annual production.

3.1 RELEASES ASSOCIATED WITH THE MAJOR USES OF EDC

Of the 4.99 million kkg of EDC produced and used in the United States in 1977, 4.81 million kkg (97%) was used as an intermediate in the production of other organic chemicals. These chemicals are: vinyl chloride monomer (85%), methyl chloroform (4.6%), ethyleneamines (3.1%), perchloroethylene (2.5%), trichloroethylene (2%), and vinylidene chloride (1%). Two percent of this EDC was used as a gasoline additive wholly as a lead scavenger. These percentages were determined from data supplied by the USITC. According to the Chemical Economics Handbook (SRI, 1975), annual growth rates for production of these chemicals has been estimated at 9% for vinyl chloride, 6% for perchloroethylene, 9% for methyl chloroform, 7% for ethyleneamines, 7% for vinylidene chloride and 7% for all others.

3.1.1 Releases of EDC Associated With the Manufacture and Use of Vinyl Chloride Monomer

In 1977, vinyl chloride was produced by the following companies: Allied Chemical, B.F. Goodrich, Borden, Continental Oil, Dow, Monochem, PPG, Stauffer, Ethyl, and Uniroyal. Most of these production plants are located in the Gulf Coast area, mainly in Texas and Louisiana

(USITC, 1978). Figure 3.1 shows the locations of vinyl chloride production plants in the United States.

The total production of vinyl chloride reported in 1977 was 2.72 million kkg (USITC, 1978); of that, 91% (or 2.48 million kkg) was produced by the EDC process (EPA, 1978). This figure is based only on the amount reported by the manufacturers. The uncertainty of this number is $\pm$ 1%.

Vinyl chloride monomer (VCM) is produced by the dehydrochlorination of EDC at high-temperature conditions and in the presence of a charcoal catalyst. The principal reaction in this process is:

$$ClCH_2CH_2Cl \xrightarrow[\text{catalyst}]{\text{heat}} CH_2 = CHCl + HCl$$

More information about this process is shown in the appendix. The overall yield of vinyl chloride in this process is from 96% to 98% (Lowenheim, Moran, 1975). Figure 3.2 shows a typical vinyl chloride production process via EDC.

As was mentioned above, the total production of vinyl chloride via the EDC process was estimated at 2.48 million kkg in 1977. Assuming that this process yields only 97% production (EPA, 1978c), the quantity of EDC needed to produce vinyl chloride in 1977 is calculated as follows:

$$\begin{pmatrix}\text{quantity of VCM}\\ \text{from EDC production}\end{pmatrix} \times \begin{pmatrix}\text{reciprocal of molecular}\\ \text{weight of VCM}\end{pmatrix}$$

$$\times \begin{pmatrix}\text{reciprocal rate of conversion}\\ \text{from EDC to VCM}\end{pmatrix} \times \begin{pmatrix}\text{molecular weight}\\ \text{of EDC}\end{pmatrix}$$

$$= \begin{pmatrix}\text{amount of EDC necessary to produce quantity}\\ \text{of VCM reported}\end{pmatrix}$$

$$(2.48 \times 10^6 \text{ kkg VCM}) \times \left(\frac{\text{kkmole VCM}}{62.45 \text{ kkg VCM}}\right) \times \left(\frac{1 \text{ kkmole EDC}}{0.97 \text{ kkmole VCM}}\right)$$

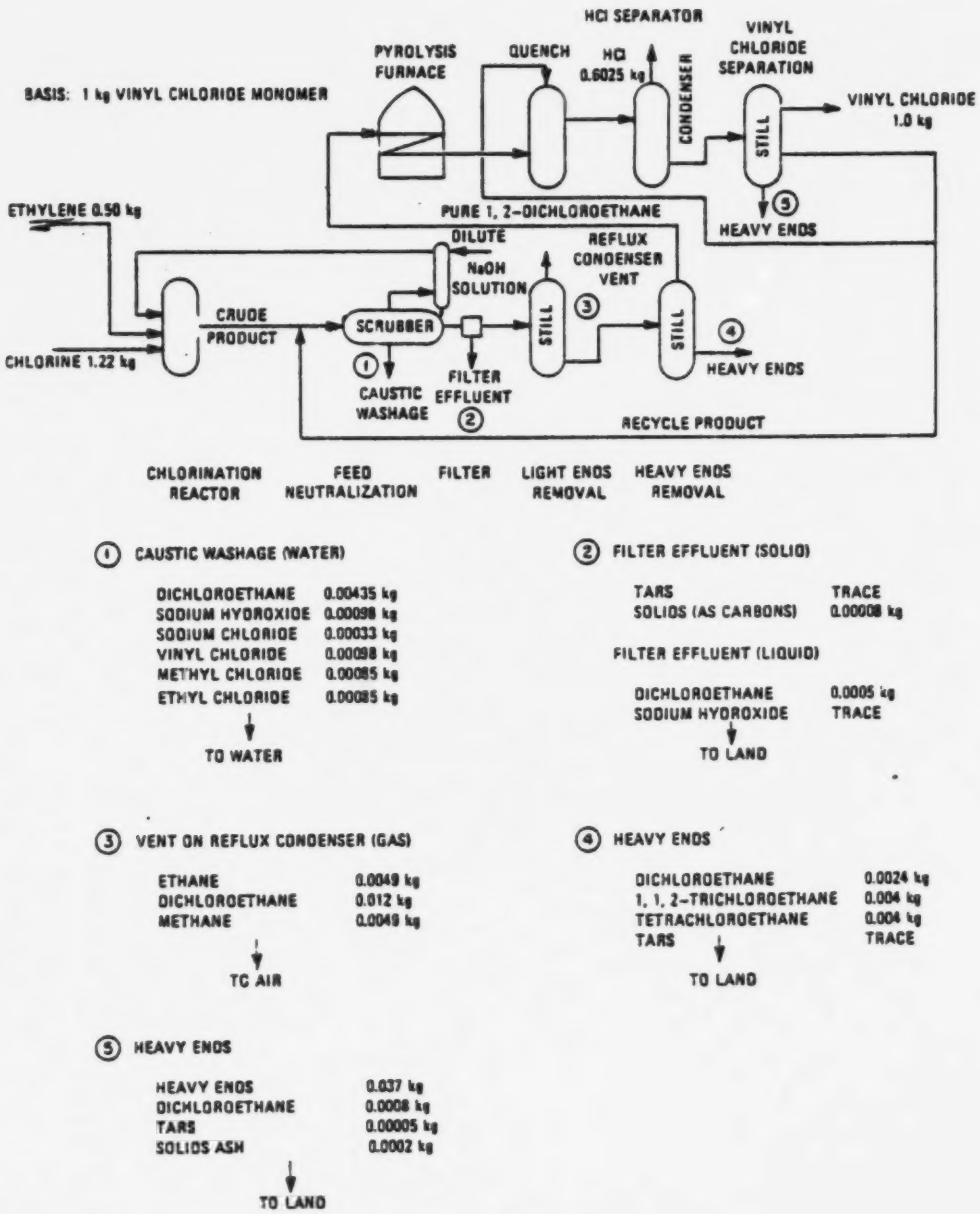
$$\times \left(\frac{98.9 \text{ kkg EDC}}{\text{kkmole EDC}}\right) = 4.05 \times 10^6 \text{ kkg EDC}$$

Company	Location	Annual Capacity, kkg	Percent
(1) Allied Chem. Corp. Indust. Chems. Div.	Baton Rouge, La.	136,200	4.3
(2) Borden Inc.* Borden Chem. Div. Petrochems.	Geismar, La	136,200	4.3
(3) Continental Oil Co. Conoco Chems. Div.	Westlake, La.	317,800	9.9
(4) Dow Chemical, U.S.A.	Freeport, Tex.	90,800	2.8
(5) Dow Chemical, U.S.A.	Oyster Creek, Tex.	317,800	9.9
(6) Ethyl Corp.	Plaquemine, La.	204,300	6.4
(7) Ethyl Corp.	Baton Rouge, La.	149,820	4.7
(8) Ethyl Corp.	Pasadena, Tex.	68,100	2.1
(9) The B.F. Goodrich Co. B.F. Goodrich Chem. Co. Div.	Calvert City, Ky	454,000	14.2
(10) Monochem, Inc.*	Geismar, La.	136,200	4.3
(11) PPG Inudst., Inc. Chem. Div. Indust. Chem. Div.	Lake Charles, La	181,600	5.7
(12) PPG Indus. (Caribe)	Guayanilla, P.R.	227,000	7.1
(13) Shell Chemical Co.	Deer Park, Tex.	381,360	11.9
(14) Shell Chemical Co.	Norco, La.	317,800	9.9
(15) Stauffer Chem. Co. Plastic Div. Resins & Compounds West	Carson, Calif.	79,450	.5
	TOTAL	3,198,430	100

*Using acetylene as feedstock

Source: EPA, 1979c

FIGURE 3.1 LOCATION OF VINYL CHLORIDE MANUFACTURING FACILITIES



Source: Gruber, 1975

FIGURE 3.2 VINYL CHLORIDE PRODUCTION PROCESS FROM EDC

The uncertainty of this number is estimated to be $\pm$ 2% because of the uncertainty of the yield rate ($\pm$ 1%) and the uncertainty of the production figures (1%). The remaining 3% of EDC is recycled in the process, emitted as waste, present as an impurity of vinyl chloride, or converted to other chlorinated hydrocarbons during the production process.

3.1.1.1 Emissions of EDC from VCM Production

In this process, major losses of EDC to the environment can occur in the effluent of aqueous heavy ends from the vinyl chloride separation unit. Stream 5 of Figure 3.2 illustrates where this release occurs. According to Gruber, this stream typically contains about 8×10^{-4} kg of EDC per kg of vinyl chloride produced (or 8×10^{-4} kkg EDC/kkg VCM) (Gruber, 1975). The uncertainty of this number is $\pm$50% because the data is not sufficient to validate Gruber's estimate. The calculated emission of EDC from the heavy-end waste stream of vinyl chloride production is:

rate of EDC emission in solid wastes x VCM production = EDC emissions in solid wastes

(0.0008 kkg EDC/kkg VCM) x (2.8×10^{6} kkg VCM) = 2.0×10^{3} kkg

The uncertainty of this figure is $\pm$51%, because of the uncertainty of production figures (1%); and 50% results from the uncertainty of the rate of EDC emissions.

According to Gruber (1975), most of the solid wastes generated from vinyl chloride manufacturing facilities were disposed of by incineration. Assuming that all of the solid wastes are incinerated and a 95%, $\pm$2% removal efficiency is achieved by incineration, 5% of EDC present in this waste stream would then be released to the atmosphere intact.

The uncertainty of this percentage is $\pm$40%. The total estimated amount of EDC released to the atmosphere in 1977 from the incineration of solid waste from vinyl chloride production was calculated as follows:

EDC emission in incineration	x	5% release to atmosphere	=	release of EDC to atmosphere from incineration of solid wastes

$$(2 \times 10^3 \text{ kkg}) \times (0.05) = 99 \text{ kkg}$$

The uncertainty of this number is +110%, -70%, because of the uncertainty of production figures ($\pm$ 1%), the uncertainty of the rate of EDC emissions in solid wastes ($\pm$ 50%), and the uncertainty of the incineration process ($\pm$ 38%).

Emissions of EDC from other sources (Streams 1, 2, 3, and 4 of Figure 3.2) have been accounted for in the production phase of EDC.

3.1.1.2 Emissions of EDC from Vinyl Chloride Monomer Uses

Estimates were made concerning the amount of residual EDC found in VCM production streams (after distillation to separate EDC from VCM).

Based on contacts with chemical producers and examination of the physical and chemical properties of EDC and VCM, it is estimated that 1-10 ppm (parts per million by weight) residual EDC would exist in VCM production streams. (Personal communication B.F. Goodrich, Borden, 1979; Mark and Gaylord, 1969). The total amount of EDC residue that would be found in VCM may be calculated as follows:

annual VCM production derived from EDC	x	estimated residue level of EDC	=	total amount of EDC found in VCM product

$$(2.5 \times 10^6 \text{ kkg}) \times 1\text{-}10 \text{ ppm (g/kkg)} = \begin{matrix} 2.5 \text{ kkg EDC at 1 ppm} \\ 25 \text{ kkg EDC at 10 ppm} \end{matrix}$$

VCM is used in the production of a wide variety of consumer products, as shown in Table 3.1. Assuming that 90% of residual EDC is destroyed in the process of manufacturing these consumer products, it is estimated that 8% of EDC is released to the environment in the production of consumer products and that 2% would be present in products

TABLE 3.1

PRODUCTS MANUFACTURED FROM EDC-DERIVED VCM

INDUSTRY	CONSUMER PRODUCT
Apparel	Baby pants
	Footwear
	Outerwear
Building and Construction Materials	Extruded foam moldings
	Flooring
	Lighting
	Panels and siding
	Pipes and fittings
	Rainwater systems
	Soffits
	Swimming pool liners
	Weather stripping
	Windows
Electrical	Wire and cables
Home Furnishings and Housewares	Appliances
	Furniture
	Garden hose
	Housewares
	Wall coverings and Wood surfacing
Packaging	Blow molded bottles
	Closure liners and gaskets
	Coatings
	Film
	Sheet
Recreation	Phonograph records
	Sporting goods
	Toys
Transportation	Auto maps
	Auto tops
	Upholstery and seat covers
Miscellaneous	Agriculture (including pipe)
	Credit cards
	Laminates
	Medical tubing
	Novelties
	Stationery supplies
	Tool and hardware

Source: US EPA, 1979c

derived from VCM. Therefore:

At 1 ppm level of impurity, EDC released to air:

(0.08) x (2.5 kkg EDC) = 0.20 kkg of EDC

At 1 ppm level of impurity, EDC retained in VCM product:

(0.02) x (2.5 kkg EDC) = 0.05 kkg of EDC

At 10 ppm level of impurity, EDC released to air:

(0.08) x (25 kkg EDC) = 2.0 kkg of EDC

At 10 ppm level of impurity, EDC retained in VCM products:

(0.02) x (25 kkg EDC) = 0.50 kkg EDC

At residue levels of 1 ppm, 0.20 kkg of EDC would be released to environment during production of consumer products, and 0.05 kkg would be present in consumer products; at 10 ppm, 2 kkg would be released to the environment, and 0.50 kkg would be present in consumer products.

3.1.2 Releases of EDC Associated with the Production and Use of Trichloroethylene

The total domestic production of trichloroethylene (TCE) in 1977 was estimated at 135 thousand kkg (USITC, 1978). This figure, obtained by the U.S. International Trade Commission, is based only on the quantities of trichloroethylene reported by manufacturing companies. The uncertainty of this number is $\pm$1%. About 90% of trichloroethylene is produced from EDC. The remaining 10% is manufactured via the chlorination of acetylene. Trichloroethylene via EDC is made in two steps: (2) chlorination of EDC to form tetrachloroethane and (b) dehydrochlorination of the latter to produce TCE (EPA, 1979). Thus the total production of trichloroethylene from the EDC process can be calculated by multiplying the total production quantity by a factor of 0.9:

$$(1.4 \times 10^{-5} \text{ kkg of TCE}) \times (0.9) = 1.2 \times 10^{5} \text{ kkg TCE}$$

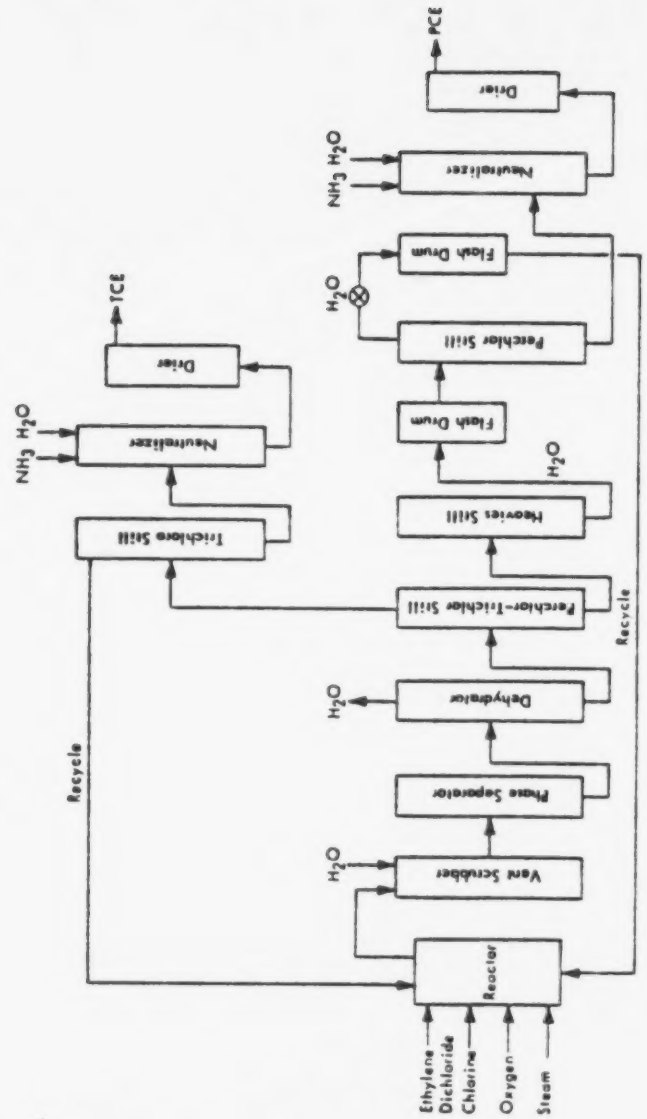
The amount of EDC used to produce 1 kg of trichloroethylene is estimated at 0.86 kg (or 0.86 kkg of EDC per kkg TCE) (EPA, 1979b). This estimate is based on an estimated 85% conversion rate of EDC to TCE. (EPA, 1979). The remaining 15% is recycled in the production

Company	Location	Capacity, kkg	Percent
(1) Diamond Shamrock Corp.	Deer Park, Tex.	40,860	14.8
(2) Dow Chem., U.S.A.	Freeport, Tex.	68,100	24.6
(3) Ethyl Corp.	Baton Rouge, La.	18,160	6.5
(4) Occidental Petroleum Corp.[a]	Taft, La.	22,700	8.2
(5) PPG Indust., Inc.	Lake Charles, La.	127,120	45.9
	TOTAL	276,940	100.0

[a]Use acetylene as feedstock.

Source: US EPA, 1979c

FIGURE 3.3 LOCATION OF TRICHLOROETHYLENE MANUFACTURING FACILITIES



Source: Lowenheim and Moran (1975)

FIGURE 3.4 PRODUCTION OF TRICHLOROETHYLENE FROM EDC

process, emitted as waste, present as an impurity in TCE, or converted to other chlorinated hydrocarbons during production of TCE. The total amount of EDC consumed by the trichloroethylene production process can then be calculated by multiplying the total production of trichloroethylene via EDC process by a factor of 0.86 of EDC per 1 kkg of trichloroethylene produced:

$$(1.2 \times 10^5 \text{ kkg TCE}) \times (0.86 \text{ kkg EDC/kkg TCE}) = 1.0 \times 10^5 \text{ kkg EDC}$$

The uncertainty of this figure is $\pm$2% due to the uncertainty of the production quantity ($\pm$1%) and the uncertainty of the conversion rate ($\pm$1%). Figure 3.3 shows the locations of the TCE production plants in the United States.

A more elaborate discussion of the production process of trichloroethylene is located in the appendix. Figure 3.4 illustrates the process for the production of trichloroethylene from EDC.

3.1.2.1 Emissions of EDC from the Production Phase of Trichloroethylene

Atmospheric emissions of EDC from the trichloroethylene production process were estimated at 600 kkg in 1976 (USEPA, 1979c); the basis for this estimate was not discussed in the report. The uncertainty of this number is $\pm$50% because of the lack of data to assess the above estimate. Information on aqueous discharge and solid waste is not available in the above report.

The estimated emission of EDC to the atmosphere in 1977 can be calculated by multiplying the emission quantity in 1976 by a factor of 1.014. The factor of 1.014 is a prorated value derived from an estimated 1.4% increase over the total consumption of EDC in 1976 (see Section 2.1). This factor will be used later in other calculations.

$$(600 \text{ kkg}) \ (1.014) = 610 \text{ kkg}$$

The uncertainty of this number is estimated to be $\pm$ 51% because of the uncertainty of the estimate of atmospheric emissions ($\pm$50%) and the uncertainty of the emission factor ($\pm$1%).

Monitoring data is needed to properly assess the sources and quantities of EDC emissions from the trichloroethylene production process. Potential sources of emissions that should be investigated include wastewater and solid waste streams.

3.1.2.2 Emission of EDC from Trichloroethylene Uses

It is estimated that EDC is present at residual levels from 1-10 ppm (parts per million, by weight) in trichloroethylene streams (personal communication, Dow Chemical, 1979). Assuming complete release of EDC to the environment during the use of trichloroethylene-derived products, the environmental release of EDC, as a result of usage of trichloroethylene-derived products, can be calculated by multiplying the total annual production of trichloroethylene (derived from EDC) by the level of residual EDC in trichloroethylene streams:

annual production of trichloroethylene derived from EDC	x	residual level of EDC in trichloroethylene streams	=	EDC release to environment

1.2×10^5 kkg x 19/kkg = 0.1 kkg at 1 ppm

1.2×10^5 kkg x 109 kkg = 1.2 kkg at 10 ppm

3.1.3 Releases of EDC Associated with the Production and Use of Perchloroethylene

Perchloroethylene (PCE) emerges as a co-product during the production of trichloroethylene. The end use for perchloroethylene is as a dry-cleaning solvent in metal cleaning and in textile finishing. The total production of perchloroethylene in 1977 was 279,000 kkg (USITC, 1978). The uncertainty of this figure is $\pm$1%. This production volume is based on the quantities reported by the manufacturers. Figure 3.5 shows the location of perchloroethylene production plants in the United States. Figure 3.6 illustrates the production process for perchloroethylene from EDC.

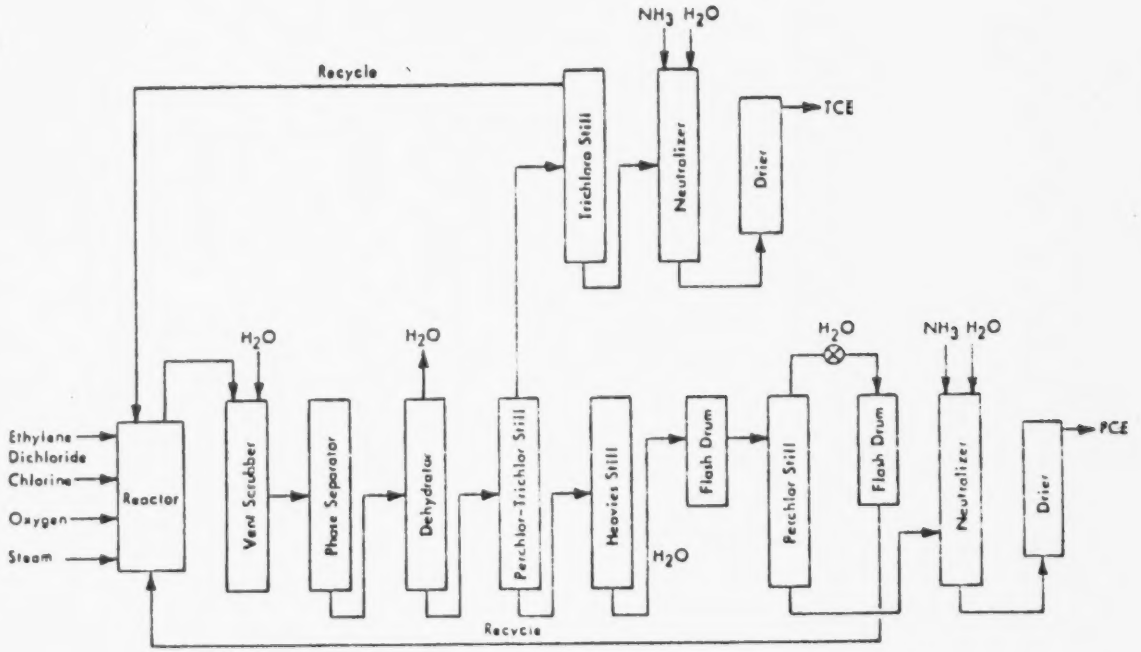
Stanford Research Institute has estimated that 6?% of perchloroethylene production uses EDC as a raw material (CEH, 1975).

Company	Location	Capacity, kkg	Percent
(1) Diamond Shamrock Corp.	Deer Park, Tex.	90,800	16.5
(2) Dow Chemical, U.S.A.	Freeport, Tex.	54,480	9.9
(3) Dow Chemical, U.S.A.	Pittsburg, Calif.	9,080	1.7
(4) Dow Chemical, U.S.A.	Plaquemine, La.	68,100	12.4
(5) E.I. DuPont de Nemours & Co.,Inc.	Corpus Christi,Tex.	72,640	13.2
(6) Ethyl Corp.	Baton Rouge, La.	22,700	4.1
(7) Occidental Petroleum Corp.*	Taft, La.	18,160	3.3
(8) PPG Indust., Inc.	Lake Charles, La.	90,800	16.5
(9) Stauffer Chem., Co.	Louisville, Ky.	31,780	5.8
(10) Vulcan Materials Co.	Geismar, La.	68,100	12.4
(11) Vulcan Materials Co.	Wichita, Kansas	22,700	4.1
	TOTAL	549,340	99.9**

*Use acetylene as feedstock.
**Deviates from 100% due to rounding

Source: US EPA, 1979c

FIGURE 3.5 LOCATION OF PERCHLOROETHYLENE MANUFACTURING FACILITIES



Source: Lowenheim and Moran (1975)

FIGURE 3.6 GENERAL PROCESS FOR PRODUCTION OF PERCHLOROETHYLENE FROM EDC

The principal reaction involved in the perchloroethylene production process via EDC method is represented as follows:

$$ClCH_2CH_2Cl + 3Cl_2 \longrightarrow Cl_2C = CCl_2 + 4HCl$$

More details about the perchloroethylene process are discussed in the appendix. It is estimated that 0.68 kg of EDC is needed to produce 1 kg of perchloroethylene (EPA, 1979b). This estimate is based on the 90% conversion rate from EDC to perchloroethylene. The remaining 10% may be recycled during the production process, emitted as waste, present in perchloroethylene as an impurity, or converted to other chlorinated hydrocarbons during production.

The amount of EDC consumed in the production of perchloroethylene in 1977 can be estimated by multiplying the total production of perchloroethylene by 0.65 and by the ratio of 0.68 kkg of EDC consumed per kkg PCE produced.

Therefore:

$(2.79 \times 10^5$ kkg PCE) (0.65) (0.68 kkg EDC/kkg PCE) = 1.2×10^5 kkg EDC

The uncertainty of this figure is also $\pm$2% (see Section 3.1.2).

3.1.3.1 Releases of EDC from the Production Process of Perchloroethylene

It is estimated that 894 kkg of EDC was released to the atmosphere from the perchloroethylene production process in 1976 (USEPA, 1979c).

The uncertainty of this number is $\pm$50% because of the lack of data to support the above estimate.

Using the escalation factor of 1.014, the total emission of EDC in 1977 from the above process can be calculated as follows:

(894 kkg) (1.014) - 910 kkg

The uncertainty of this figure is $\pm$51% because of the uncertainty of emission during the production process ($\pm$50%) and the uncertainty of the emission factor ($\pm$1%).

The production process of perchloroethylene from acetylene has also been studied (Gruber, 1975).

Figure 3.7 illustrates the production process of perchloroethylene from acetylene. As pointed out by Gruber, EDC is emitted to the air from the chlorinator reactor reflux condenser equipment of this process (stream 3). The released quantity is estimated at 0.00245 kg of EDC per kg of perchloroethylene produced. The uncertainty of this number is $\pm$50% because of the lack of data to assess the above estimate.

Using this estimation, the emission of EDC from this source to the air can be calculated by multiplying the total acetylene-based production of perchloroethylene by 0.00024.

Therefore:

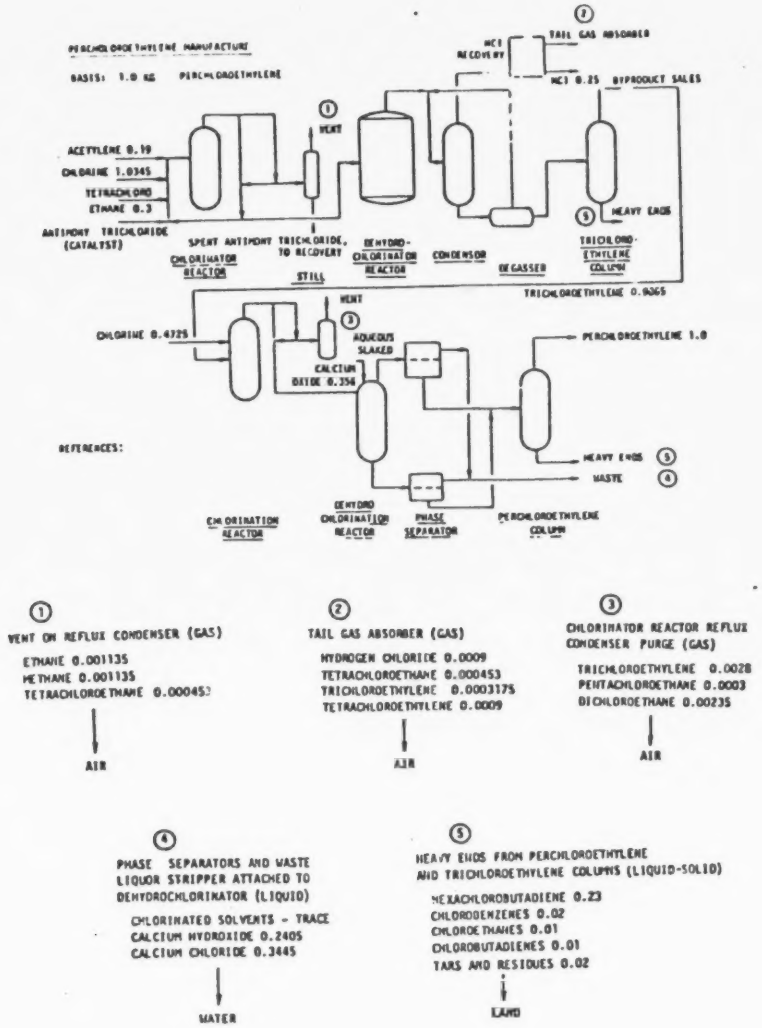
$(8.4 \times 10^3$ kkg of PCE) x (0.0024 kkg EDC/kkg PCE) = 20 kkg EDC

The uncertainty of this figure is $\pm$51% because of the uncertainty of EDC emissions during the production process of perchloroethylene from acetylene ($\pm$50%) and the uncertainty of the quantity of perchloroethylene produced ($\pm$1%).

Traces of EDC can be found in the heavy ends from the perchloroethylene column, but monitoring data is needed to estimate the quantity of EDC present in the waste streams.

Although monitoring data from the acetylene-based and the EDC-based production processes of perchloroethylene do not reveal EDC in wastewater discharge (Gruber 1975, EPA 1979), it is suspected that airborne emission of EDC could occur during wastewater treatment because of its high volatility. Therefore, air emission from aquatic discharge should be investigated in further studies.

Solid wastes discharged by both mentioned production processes do not contain EDC (EPA, 1979, Gruber 1975). Again, this source of emission should be verified in further studies.



Source: Gruber, 1975

FIGURE 3.7 PRODUCTION OF PERCHLOROETHYLENE VIA THE ACETYLENE METHOD

3.1.3.2 Emission of EDC from Perchloroethylene Uses

It is estimated that perchloroethylene streams contain impurities of EDC from 1-10 ppm (part per million, by weight, personal communication, Dow Chemical, 1979). The uses of perchloroethylene include textile cleaning, metal degreasing, fluorocarbon manufacture and solvent in textile processing. The use of products derived from perchloroethylene can thus result in the environmental release of EDC. To quantify the environmental release of EDC from perchloroethylene-derived products, the total annual production of perchloroethylene derived from EDC is multiplied by the level of EDC residue in perchloroethylene streams. It is assumed that there is complete release to the environment of EDC during usage of perchloroethylene-derived products. Therefore:

total annual production of perchloroethylene derived from EDC	x	residue levels of EDC in perchloroethylene streams	=	environmental release of EDC

1.8×10^5 kkg x 1 g/kkg = 0.2 kkg at 1 ppm

1.8×10^5 kkg x 10 g/kkg = 1.8 kkg at 10 ppm

3.1.4 Releases of EDC Associated with the Production and Use of Vinylidene Chloride

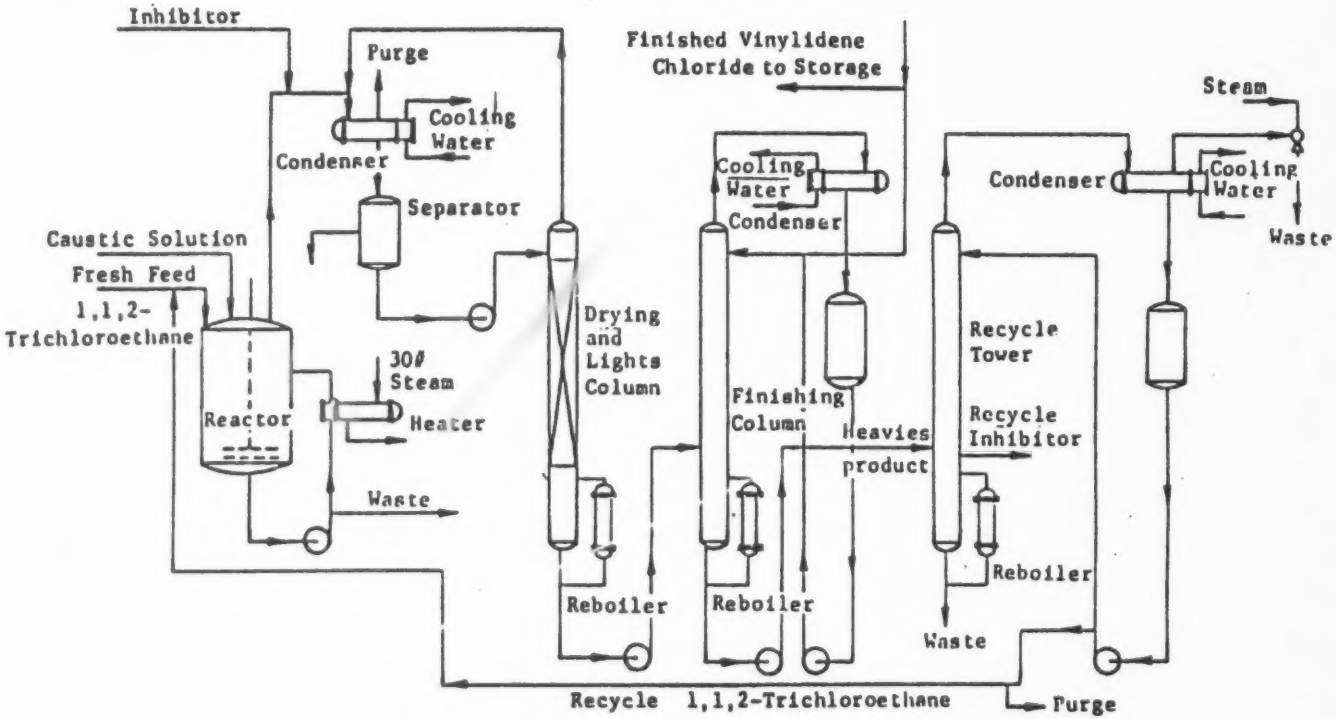
Vinylidene chloride (VDC) was produced in 1977 by Dow Chemical Company and PPG, Inc. The plant locations are illustrated in Figure 3.8. According to SRI (1975), the total production of vinylidene chloride in 1977 was estimated at 105,000 kkg. Of that, 62,500 kkg was used in the production of methyl chloroform (see Section 3.1.5). It is difficult to validate the total production figure of vinylidene chloride. The production quantities of vinylidene chloride were reported to the U.S. International Trade Commission. These figures could not be released to the public, since the USITC policy prohibits such release when there are three or fewer producers.

The production process of vinylidene chloride is shown in the appendix. Figure 3.9 shows a typical production process of vinylidene

	Company	Location
(1)	Dow Chemical U.S.A.	Freeport, Tex.
(2)	Dow Chemical U.S.A.	Plaquemine, La.
(3)	PPG Indust., Inc.	Lake Charles, La.

Source: EPA, 1979c

FIGURE 3.8 LOCATION OF VINYLIDENE CHLORIDE MANUFACTURING FACILITIES



Source: US EPA, 1978c

FIGURE 3.9 PRODUCTION OF VINYLIDENE CHLORIDE

chloride. The principal reaction involved in the process is:

$$CH_2ClCHCl_2 + NaOH \longrightarrow CH_2 = CCl_2 + NaCl + H_2O$$

Vinylidene chloride is formed in two steps: (a) chlorination of EDC to produce 1,1,2-trichloroethane, and (b) dehydrochlorination of the latter to produce vinylidene chloride. For the purpose of this materials balance, it is estimated that 1.18 kg of EDC is needed to produce 1 kg of vinylidene chloride. This estimate is based on a 96% conversion rate from EDC to 1,1,2-trichloroethane. The uncertainty of this number is estimated to be $\pm$2% because of the lack of information on yield rate.

The total amount of EDC consumed in vinylidene chloride production in 1977 can be calculated by multiplying the production quantity by the ratio of 1.18 kg of EDC consumed per kg of vinylidene chloride produced:

$$1.05 \times 10^5 \text{ kkg VDC } (1.18 \frac{\text{kkg EDC}}{\text{kkg VCE}}) = 1.2 \times 10^5 \text{ kkg EDC}$$

The uncertainty of this number is $\pm$3% because of the uncertainty of yield rates (2%) and the uncertainty of production figures (1%).

The quantity of EDC used in the production of methyl chloroform using vinylidene chloride as intermediate is estimated at 74,000 kkg in 1977 (see Section 3.1.5). Thus, the quantity of EDC used for the total consumption in vinylidene chloride production can be calculated by subtracting the amount of EDC consumed in the production of the vinylidene chloride used as an intermediate in the manufacture of methyl chloroform from the amount of EDC used in the total production of vinylidene chloride:

$$(1.2 \times 10^5 \text{ kkg EDC}) - (7.4 \times 10^4 \text{ kkg EDC}) = 4.6 \times 10^4 \text{ kkg EDC}$$

The uncertainty of this figure is estimated to be $\pm$3%.

3.1.4.1 Emission of EDC from the Manufacturing Process of Vinylidene Chloride

In a report obtained from EPA, an atmospheric emission of 594 kkg of EDC was estimated in 1976 from the vinylidene chloride production facilities (USEPA, 1979c). The uncertainty of this number is $\pm$50% because of the lack of data to assess the above estimate. Using the escalation factor of 1.014 for 1977, the estimated total emission of EDC from this process is calculated by multiplying the 1976 emission figure (594 kkg) by the escalation factor (1.014):

$$(594 \text{ kkg}) \times (1.014) = 600 \text{ kkg}$$

The uncertainty of this figure is $\pm$51% because of the uncertainty of EDC emissions during the manufacture of vinylidene chloride ($\pm$50%) and the uncertainty of the emission factor ($\pm$1%).

For the purpose of this materials balance, it is also suggested that the wastewater stream from the manufacturing process for vinylidene chloride is a common source of airborne emission of EDC. Monitoring data is needed to properly assess the quantity of EDC released by this source.

According to Figure 3.9, heavy-ends waste or solid waste streams are not identified in the production process of vinylidene chloride. Therefore, it is assumed that there are none.

3.1.4.2 Emission of EDC from Uses of Vinylidene Chloride

It is estimated that EDC is present at residual levels from 1-10 ppm (parts per million, by weight, personal communication Aldrich Chemical Company, 1979) in vinylidene chloride streams. The uses of vinylidene chloride include VDC polymer, packaging film, coating for packaging materials, flame-resistant fiber, and coating for textiles, carpets, nonwovens and paper. Assuming complete release of EDC to the environment during the use of vinylidene chloride-derived products, the environmental release of EDC as a result of usage of products derived from vinylidene chloride can be calculated by multiplying the total annual production of vinylidene chloride (derived from EDC) by

the level of residual EDC in vinylidene chloride streams:

annual production of vinylidene chloride derived from EDC	x	residual level of EDC in trichloroethylene streams	=	EDC release to environment

$$4.3 \times 10^4 \text{ kkg} \times 1 \text{ g/kkg} = 0.04 \text{ kkg at 1 ppm}$$

$$4.3 \times 10^4 \text{ kkg} \times 10 \text{ g/kkg} = 0.4 \text{ kkg at 10 ppm}$$

3.1.5 Releases of EDC Associated with the Production and Use of Methyl Chloroform

It is estimated that 60% of the production of methyl chloroform (MC) is derived from vinyl chloride and 30% is based on the use of vinylidene chloride as raw material (EPA, 1979). The total production of methyl chloroform in 1977 was estimated at 288,000 kkg (USITC, 1978). The uncertainty of this number was estimated to be $\pm$1%. The remaining 10% of methyl chloroform is a derivation from ethane rather than a product of EDC. There are no documented EDC emissions related to this process. This production is based solely on the quantities of methyl chloroform reported by the manufacturers. The total production of methyl chloroform from the vinyl chloride method can be calculated by multiplying the annual total production quantity by 60%.

$$(2.88 \times 10^5 \text{ kkg}) (0.60) = 1.7 \times 10^5 \text{ kkg} \quad (1)$$

The uncertainty of this number was estimated to be $\pm$1%.

The amount of methyl chloroform produced from the vinylidene chloride method can also be calculated by multiplying the total production of methyl chloroform in 1977 by 30%.

$$(2.88 \times 10^5 \text{ kkg}) (0.30) = 8.6 \times 10^4 \text{ kkg} \quad (2)$$

The uncertainty of this number was estimated to be $\pm$1%.

Production plants for methyl chloroform are located mainly along the Gulf Coast of the United States (Figure 3.10).

	Company	Location	Annual Capacity, kkg	Percent
(1)	Dow Chemical U.S.A.	Freeport, Tex.	204,300	65.2
(2)	PPG Indust., Inc.	Lake Charles, La.	79,450	25.4
(3)	Vulcan Materials Co.*	Geismar, La.	29,510	9.4
		TOTAL	313,260	100.0

*Using ethane as feedstock

Source: US EPA, 1979c

FIGURE 3.10 LOCATION OF METHYL CHLOROFORM MANUFACTURING FACILITIES

A typical production process of methyl chloroform using vinyl chloride as raw material is discussed in greater detail in the appendix. Figure 3.11 shows a typical methyl chloroform production process from the vinyl chloride method.

$$CH_2 = CHCl + HCl \longrightarrow C_2H_6Cl_2 \quad (3)$$

$$C_2H_2Cl_2 + Cl_2 \xrightarrow{(400^oC)} CH_3CCl_3 + HCl \quad (4)$$

It is estimated that 0.5 kg vinyl chloride is needed to produce 1 kg of methyl chloroform (Gruber, 1975). This estimate is based on an estimated 95% conversion rate of vinyl chloride to methyl chloroform (Lowenheim and Moran, 1975). The uncertainty of this number was estimated to be $\pm$1%.

The total amount of vinyl chloride consumed to produce 173,000 kkg of methyl chloroform can then be calculated by multiplying this amount by a ratio of 0.5 kkg vinyl chloride per kkg of methyl chloroform:

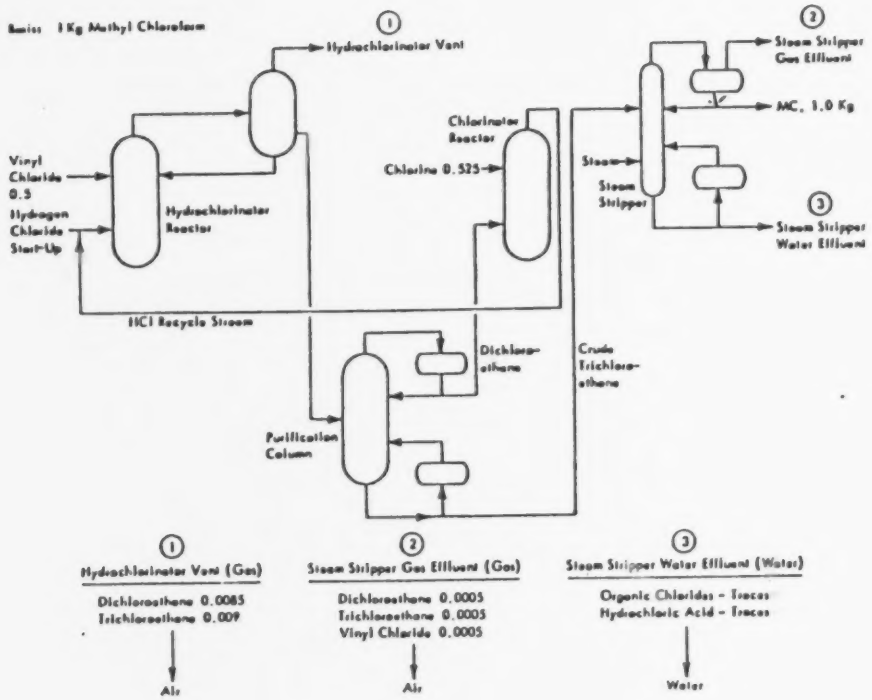
$$(1.73 \times 10^5 \text{ kkg MC}) \times (0.5 \frac{\text{kkg VCM}}{\text{kkg MC}}) = 8.65 \times 10^4 \text{ kkg VCM} \quad (5)$$

The uncertainty of this number was estimated to be $\pm$2%.

The U.S. International Trade Commission does not report the amount of vinyl chloride that is produced from EDC for the manufacture of methyl chloroform. Therefore, it is necessary to calculate the quantity of EDC used to produce 865,000 kkg of vinyl chloride as intermediates in the manufacturing process of methyl chloroform. This quantity can be calculated by (a) multiplying the quantity of vinyl chloride by the molecular weight of EDC, and (b) dividing by the molecular weight of vinyl chloride and by the ratio of 0.96 mole of vinyl chloride produced per mole of EDC consumed (See Section 3.1.1):

$$\frac{(8.6 \times 10^4 \text{ kkg VCM}) \times (98.9 \frac{\text{kkg EDC}}{\text{kkmole EDC}})}{(62.45 \frac{\text{kkg VCM}}{\text{kkmole VCM}}) \times (\frac{0.98 \text{ kkmole VCM}}{\text{kkmole EDC}})} = 1.4 \times 10^5 \text{ kkg of EDC} \quad (6)$$

The uncertainty of this figure was estimated to be $\pm$3%.



Source: Gruber, 1975

FIGURE 3.11 PRODUCTION OF METHYL CHLOROFORM FROM VINYL CHLORIDE

As mentioned above, methyl chloroform may also be produced by the vinylidene process. The quantity of methyl chloroform produced by this process is estimated at 86,000 kkg in 1977. Figure 3.12 shows a typical process of methyl chloroform production via the vinylidene chloride method. The basic reaction in this process is:

$$CH_2 = CCl_2 + HCl \xrightarrow{FeCl_3} CH_3CCl_3 \qquad (7)$$

Methyl chloroform is formed by the hydrochlorination of vinylidene chloride in the presence of $FeCl_3$ catalyst. More information pertaining to the vinylidene chloride-based methyl chloroform production process is given in the appendix.

The amount of vinylidene chloride used to produce 86,000 kkg of methyl chloroform in 1977 can be calculated by multiplying the quantity of methyl chloroform by a factor of 0.73 kg of vinylidene chloride used per kg of methyl chloroform produced (EPA, 1979b):

$$(86 \times 10^3 \text{ kkg MC}) \times (0.73 \frac{\text{kkg VCC}}{\text{kkg MC}}) = 6.3 \times 10^4 \text{ kkg VDC} \qquad (8)$$

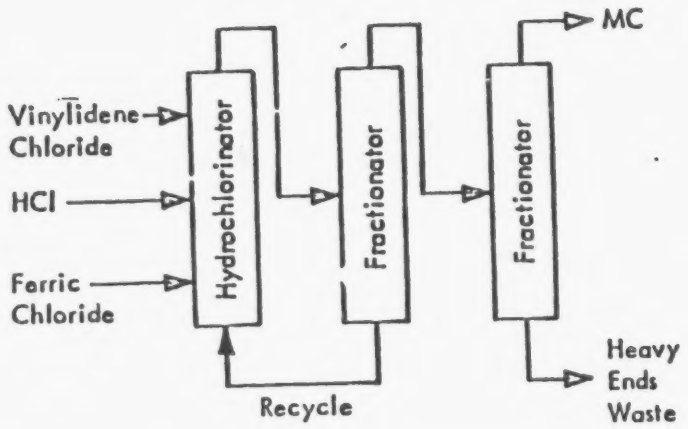
A 99.5% yield from Reaction (7) is estimated from the ratio of the amount of vinylidene chloride used (0.73 kg) per kg of methyl chloroform produced. The theoretical yield of methyl chloroform from Reaction (7) is over 98% (Lowenheim and Mora, 1975).

The amount of EDC consumed in the methyl chloroform production process using vinylidene chloride as intermediate can thus be calculated by multiplying the calculated vinylidene chloride needed for the methyl chloroform production by the ratio of 1.26 kg of EDC consumed per kg of vinylidene produced (see Section 3.1.4):

$$(6.3 \times 10^4 \text{ kkg VDC}) \times (1.18 \frac{\text{kkg EDC}}{\text{kkg VDC}}) = 7.4 \times 10^4 \text{ kkg EDC} \qquad (9)$$

The total quantity of EDC consumed by both methyl chloroform production processes in 1977 (the vinyl chloride-based and the vinylidene chloride-based) can then be calculated by taking the sum of Equation (6) and Equation (9):

$$(1.4 \times 10^5 \text{ kkg EDC}) + (7.4 \times 10^4 \text{ kkg EDC}) = 2.1 \times 10^5 \text{ kkg EDC}$$



Source: Lowenheim and Moran (1975).

FIGURE 3.12 PRODUCTION OF METHYL CHLOROFORM FROM VINYLIDENE CHLORIDE

3.1.5.1 Emissions of EDC from the Production Processes of Methyl Chloroform

Figure 3.11 shows the gas and liquid waste stream for the methyl chloroform production process from the vinyl chloride method. The two major sources of EDC emission to the atmosphere from the vinyl chloride-based production process of methyl chloroform are: (a) the hydrochlorinator vent, and (b) the steam stripper gas effluent (Streams 1 and 2 of Figure 3.11). Based on 1 kg of methyl chloroform produced, the quantities of EDC released from Stream 1 and Stream 2 of Figure 3.11 are, respectively, 0.0085 kg and 0.0005 kg (Gruber, 1975). Thus the amount of EDC emission to air from the vinyl chloride-based process is 0.009 kg of EDC per kg of methyl chloroform produced. The uncertainty of this number is estimated to be $\pm$50% because of the lack of data necessary to assess EDC emissions.

The total amount of EDC emission to the air in 1977 from the raw material can then be calculated by multiplying the methyl chloroform production from vinyl chloride [Equation (1)] by the ratio of 0.009 kg of EDC released per kg of methyl chloroform produced:

$$(173 \times 10^3 \text{ kkg MC}) \left(0.009 \frac{\text{kkg EDC}}{\text{kkg MC}}\right) = 1.6 \times 10^3 \text{ kkg}$$

The uncertainty of this number is $\pm$51% because of the following factors:

- the uncertainty of methyl chloroform production figures ($\pm$1%)
- the uncertainty of EDC emissions during production of methyl chloroform ($\pm$50%).

Analysis of water samples from the vinyl chloride-based production process of methyl chloroform does not show any trace of EDC (Gruber, 1975). Because of the high volatility of EDC, atmospheric emissions from the aquatic discharge from the production facilities should be investigated in later studies.

No land-destined solid wastes are discharged by the vinyl chloride-based process (Gruber, 1975).

Information on EDC emissions from the vinylidene chloride-based production process of methyl chloroform is not available. It is suspected that EDC could be present in the heavy-ends waste stream and the aqueous effluent waste stream discharged by the vinylidene chloride-based process. More information is needed to quantify the amount of EDC released from these sources.

3.1.5.2 Emission of EDC from Methyl Chloroform Uses

It is estimated that methyl chloroform streams contain impurities of EDC from 1-10 ppm (part per million, by weight, personal communication, J. T. Baker Company, 1979). Methyl chloroform is used as a degreaser, aerosol depressant, solvent, coolant and lubricant in cutting oil. The use of products derived from methyl chloroform can result in the environmental release of EDC. To quantify the environmental release of EDC from methyl chloroform-derived products, the total annual production of methyl chloroform derived from EDC is multiplied by the level of EDC residue in methyl chloroform streams. It is assumed that there is complete release to the environment of EDC during use of methyl chloroform-derived products. Therefore:

total annual production of methyl chloroform derived from EDC	x	residue levels of EDC in methyl chloroform streams	=	environmental release of EDC

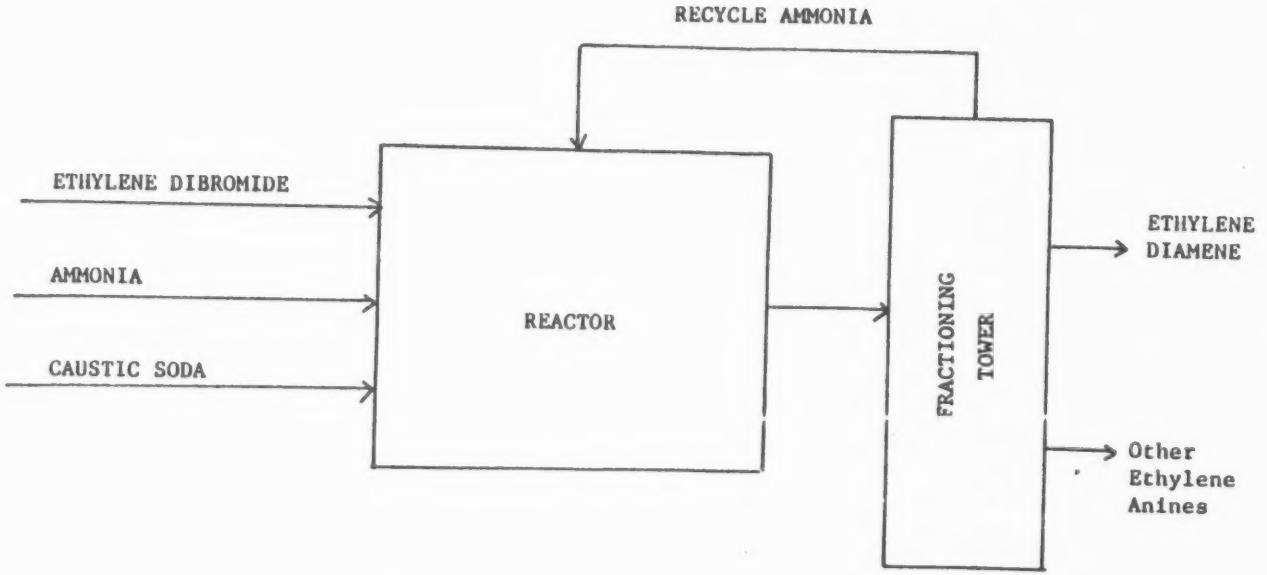
$$260 \times 10^3 \text{ kkg} \times 1 \text{ g/kkg} = 0.3 \text{ kkg at 1 ppm}$$
$$260 \times 10^3 \text{ kkg} \times 10 \text{ g/kkg} = 2.6 \text{ kkg at 10 ppm}$$

3.1.6 Releases of EDC Associated with the Production and Use of Ethyleneamines

Ethyleneamines (EA) are produced by reacting EDC with ammonia. The basic reaction in this process is:

$$ClC_2H_4Cl + 2NH_3 \longrightarrow NH_2(CH_2)_2NH_2 + 2HCl + \text{other ethyleneamines}$$

Yield of this process depends heavily on the reaction conditions (Lowenheim and Moran, 1975). Figure 3.13 shows a simplified production process for ethyleneamines.



Source: Lowenheim and Moran (1975)

FIGURE 3.13 PRODUCTION OF ETHYLENEAMINES FORM EDC

According to SRI (1975), 59,875 kkg of ethyleneamines were estimated to have been produced in 1974. Based on an estimated 5% increase per year in the production of ethyleneamines, the total increase in the production of ethyleneamines in 1977 over that in 1974 will be:

First year: 5% of 100% = 105%
Second year: 5% of 105% = 110.25%
Third year: 5% of 110.25% = 115.76%

The total production of ethyleneamines in 1977 can then be calculated by multiplying the total production of ethyleneamines in 1974 by a factor of 1.158:

$$(59{,}875 \text{ kkg}) \times (1.158) = 6.9 \times 10^4 \text{ kkg}$$

The uncertainty of this number is estimated to be $\pm$5%.

Ethyleneamines are produced by Dow Company and Union Carbide plants located in Texas and Louisiana. Figure 3.14 shows the locations of these manufacturing plants.

It is estimated that 2.2 kg of EDC is needed to produce 1 kg of ethyleneamines (SRI, 1975). The uncertainty of this number is estimated to be $\pm$2% because the above estimate was not defined in the report. The total amount of EDC can then be calculated by multiplying the estimated total production of ethyleneamines in 1977 by the ratio of 2.2 kg of EDC consumed per kg of ethyleneamines produced:

$$\left(2.2 \frac{\text{kkg EDC}}{\text{kkg EA}}\right) \times (6.9 \times 10^4 \text{ kkg}) = 1.5 \times 10^5 \text{ kkg EDC}$$

The uncertainty of this number is estimated to be $\pm$10% because of the uncertainty of the production of ethyleneamines ($\pm$5%) and the uncertainty of the amount of EDC needed to produce 1 kg of ethyleneamines ($\pm$2%).

3.1.6.1 Emissions of EDC from the Production Process of Ethyleneamines

The estimated emissions of EDC from the ethyleneamine production facilities was 600 kkg in 1976 (USEPA, 1979c). The uncertainty of this number is estimated to be $\pm$50% because of the lack of data necessary

	Company	Location	Capacity, kkg	Percent
(1)	Dow Chem., U.S.A.	Freeport, Tex.	13,620	32.3
(2)	Union Carbide Corp.	Taft, La.	17,706	41.9
(3)	Union Carbide Corp.	Texas City, Tex.	10,896	25.8
		TOTAL	42,222	100.0

Source: US EPA, 1979c

FIGURE 3.14 LOCATION OF ETHYLENEAMINES MANUFACTURING FACILITIES

to assess the above estimate.

The estimated total emission of EDC to the air in 1977 from the ethyleneamines production facilities is calculated by multiplying the emission quantity in 1976 (600 kkg) by the escalation factor of 0.014 for 1979 (see Section 3.1):

$$(600 \text{ kkg})\ (1.014) = 610 \text{ kkg}$$

The uncertainty of this number is $\pm$51% as a result of the following factors:

- the uncertainty of the emission of EDC from ethyleneamine production ($\pm$50%)
- the uncertainty of the escalation factor ($\pm$1%).

Like the other chemical intermediate production processes, such as the vinyl chloride-based methyl chloroform production process, it is suspected that EDC emissions can occur in wastewater streams and solid waste streams discharged by the production process of ethyleneamines. More information is needed to determine properly the quantities of EDC emitted from these sources.

3.1.6.2 Emissions of EDC from Ethyleneamine Uses

Ethyleneamines are used in producing carbamate fungicides, chelating agents, dimethylethylene urea resins, and diaminoethylethanol. It is estimated that EDC is present at residual levels from 1-10 ppm (parts per million, by weight, personal communication, Dow, 1979) in ethyleneamine streams. Assuming complete release of EDC to the environment during the use of ethyleneamine-derived products, the environmental release of EDC, as a result of usage of ethyleneamine-derived products, can be calculated by multiplying the total annual

production of ethyleneamine (derived from EDC) by the level of residual EDC in ethyleneamine streams:

annual production of ethyleneamine derived from EDC	x	residual level of EDC in ethyleneamine streams	=	EDC release to environment

$$6.9 \times 10^4 \text{ kkg} \times 1 \text{ g/kkg} = 0.07 \text{ kkg at 1 ppm}$$

$$6.9 \times 10^4 \text{ kkg} \times 10 \text{ g/kkg} - 0.07 \text{ kkg at 10 ppm}$$

3.1.7 Releases of EDC Associated with Its Use as a Leaded Gasoline Additive

EDC is used in conjunction with 1,2-dibromoethane as a lead scavenger in leaded gasoline. EDC is added to leaded gasoline to provide cleaner burning of the lead anti-knock compounds in the engine. It is estimated that a typical gallon of leaded gasoline contains approximately 2.5 grams of lead per gallon or 0.66 grams of lead (0.0032 moles) per liter (EPA, 1979a), based on conclusions drawn from a report by Mara and Lee (1978). Since two atoms of chlorine are available in EDC for each atom of lead in the gasoline, 0.32 grams of EDC (0.0032 moles) are added to each liter of leaded gasoline. In 1977, 1,899,166,000 barrels, or 3.015×10^{11} liters, of leaded gasoline were produced in the United States (API personal communication, October 3, 1979). All leaded gasoline is assumed to contain EDC as a lead scavenger.

The total EDC used as a lead scavenger in gasoline in 1977 is calculated by multiplying the amount of leaded gasoline produced in 1977 ($3.015 \times 3.0 \times 10^{11}$ liters) by the amount of EDC in a liter of gasoline (grams/liter):

$$(3.015 \times 10^{11})\ (0.32) = 9.7 \times 10^{10} \text{ grams}$$

or

$$9.7 \times 10^4 \text{ kkg}$$

Since there was no data to calculate EDC emissions from gasoline-blending operations, for the purposes of this materials balance, JRB estimates that the EDC emissions are 0.1% of EDC in the processed gasoline. These emissions are primarily air emissions:

$$(9.56 \times 10^4) \times (0.001) = 97 \text{ kkg EDC/year}$$

The uncertainty of this number is estimated to be $\pm$100% because of the lack of data to estimate EDC emissions from gasoline.

3.1.7.1 Emissions of EDC from Gasoline

Releases of EDC from leaded gasoline to the environment occur before and during combustion. No emissions of EDC occur after combustion, since EDC is destroyed during the ignition and combustion of the fuel. Emission of EDC occurs through four main vehicles:

- tank breathing
- vapor displacement (filling losses)
- spills, leaks and fugitive emissions
- combustion.

a. Emissions from Tank Breathing

Gasoline and EDC are released from fixed roof or fixed volume storage tanks even when there is not transfer activity. Temperature-induced pressure differentials expel vapor and air as the temperature increases and draw fresh air into the tank as the temperature decreases. These releases of vapor and air are referred to as tank breathing or breathing losses. Floating roof tanks and highly pressurized tanks that are more common to refineries and very large storage sites do not emit the breathing releases associated with fixed roof tanks and are excluded from EDC emission considerations. The greatest number of fixed roof gasoline tanks are found in bulk gasoline plants (EPA, December, 1977).

The 1972 Census of Business indicates that there were 23,367 bulk plants in the U.S. The number of these bulk plants has been decreasing in recent years, with an 11% decrease from 1967 to 1972. Therefore, for the purposes of this emission estimate, the number of bulk plants in 1972 is reduced by 15% to account for the decrease through 1977, providing a base of 19,862 plants.

Additionally, 30% of these 19,862 facilities are underground storage facilities, which further reduces the number of bulk plants

under consideration to 13,903. The typical gasoline bulk plant (EPA, 1977b) contains three tanks between 50,000 and 75,000 liters. We assume each tank is estimated to lose 3 kg/day to breathing losses. It is estimated that each bulk plant will have two tanks for leaded gasoline.

The estimated breathing losses of EDC are calculated by multiplying the daily hydrocarbon (gasoline, emissions per tank (3 kg/day/tank) by the number of facilities with above-ground tanks (13,903) by the number of tanks in a typical facility that contain leaded gasoline (2) by the quantity (liters) of gasoline in a kg (1.5) by the amount of EDC (grams) in a liter of gasoline (0.32) by the number of days in a year (365). The product is divided by 10^6 to convert the answer to grams of EDC to kkg.

(3 kg/day/tank) x (13,903 facilities) x (2 tanks/facility) x (1.15 liters gasoline/kg) x (0.32 grams EDC/liter gasoline) x (365 days/year) ÷ (1 kkg/10^6 grams) = 11.0 kkg/year

For this calculation, gasoline vapor and gasoline liquid compositions were assumed to be the same. This assumption will increase the EDC emission estimate slightly because gasoline is slightly more volatile than EDC.

b. Emissions of EDC from Vapor Displacement (Tank Filling Losses)

Emissions of EDC and miscellaneous hydrocarbons also occur during the filling of fixed roof or fixed volume tanks. The hydrocarbon vapor above the gasoline is forced into the atmosphere during the filling of the tanks and is not usually drawn back in as the tank is drawn down. These losses typically occur to some extent during all transfer operations. EDC is discharged in small quantities with the gasoline proper, thus providing a route for environmental vapor emissions, principally to the air.

Filling operations emissions can be controlled by vapor balance systems, hydrocarbon oxidation systems and refrigerated vent systems. These emission control systems typically reduce tank filling losses and

emissions by approximately 80%.

The following calculations estimate the EDC emissions from gasoline tank filling operations in 1977.

The following conditions are assumed or are known for the EDC emission calculations:

- In 1977, 1,899,166,000 barrels of leaded gasoline were produced and distributed (API personal communication, October 3, 1979)
- The total volume of gasoline distributed is turned over three times during shipment and storage (assumption)
- The raw emissions from 25% of the transfer operations are reduced by 80% by emission control devices
- The displaced air and vapor leave the tanks saturated at $60^{\circ}F$ ($15.6^{\circ}C$) (assumption)
- The EDC content of gasoline is 1.2 gram (9.012 mole) per gallon or 1.04 mole % (EPA 1979)
- Vapor pressure of EDC @ $60^{\circ}F$ is 48.7 mmHg or 0.06 atm (Perry Chemical Engineering Handbook)
- Vapor pressure of gasoline at $60^{\circ}F$ is 61.8 mmHg (Perry Chemical Engineering Handbook).

The first step in calculating the EDC emissions from a gasoline tank filling operation is to calculate the volume of gasoline vapor (ft^3) needed per lb-mole of EDC vapors. The vapor volume is calculated by multiplying the molar volume of a gas (359 ft^3/lb-mole) by a temperature ratio (520/460) to convert the molar volume to $60^{\circ}F$, which is the escaping vapor temperature. The product is then divided by the molar ratio of EDC to gasoline (0.0004) and by the vapor pressure of EDC in atmospheres at $60^{\circ}F$ (0.064 atm).

$$\frac{(359\ ft^3\ lb/mole\ at\ STP) \times \left(\frac{520^{\circ}R}{460^{\circ}R}\right)}{(0.0004\ mole\ EDC/mole\ gasoline)\ (0.06\ atm\ @\ 60^{\circ}F)} =$$

$$16{,}909{,}420\ ft^3\ lb\text{-}mole\ of\ EDC\ vapor\ in\ air$$

The next step is to calculate the volume of vapor and air emitted during tank filling operations in 1977. To calculate this volume, the total supply of leaded gasoline (1,899,166,000 barrels/year) is

multiplied by the number of cubic feet in a barrel (5.61 ft^3/barrel) and by the number of times the total volume is assumed to be transferred during distribution (3 turnovers):

(1,899,166,000 barrels/year) (5.61 ft^3/barrel) (3 turnovers) =

3.2×10^{10} ft^3 vapor/year

The amount of uncontrolled EDC vapor emissions is then calculated by dividing the total volume of vapor and air emitted during tank filling operations in 1977 (3.196×10^{10} ft^3 year) by the cubic feet of vapor needed for 1 lb-mole of EDC (1.69×10^7 ft^3/lb-mole) and that product is multiplied by the number of kg of EDC in a lb-mole (44.5 kg EDC/lb-mole).

No emission control: $\frac{3.2 \times 10^{10} ft^3 \text{ vapor/year } (44.5 \text{ kg EDC/lb-mole}}{1.69 \times 10^7 \text{ } ft^3\text{/lb-mole}} =$

84 kkg EDC/year

A more realistic estimate of tank filling losses is obtained when the above 84,080 kg quantity of EDC emissions is reduced to reflect an emission control of 25% of all transfer operations (0.75) (84,080 kg) and an 80% reduction in emissions for those facilities that use emission control (0.25) (84,080) (.20).

With emission control:

$[(0.75) \times (84,260)] + [(0.25) \times (84,260) \times (.20)] = 67$ kkg EDC/year

c. Emissions of EDC from Spills, Leaks, and Fugitive Emissions of Gasoline

The impact of these miscellaneous emissions on the quantity of environmental EDC is not believed to be significant. The overall quantity of EDC in gasoline is quite small, and the discharge of gasoline is usually minimized as much as possible.

Emissions of EDC from gasoline will undoubtedly be reduced in the future. In 1977, leaded gasoline accounted for 72.5% of all motor fuel. In 1978, leaded gasoline accounted for 66.1% of all motor fuel, and

during the first six months of 1979 leaded fuel accounted for 61.7% of production (API personal communication, October 3, 1979). Recent trends and future requirements for the use of unleaded fuels indicate that the total demand for leaded fuels is diminishing. Therefore, the use of EDC in leaded fuels is also decreasing. The estimates of EDC emissions from gasoline could be refined, but the current trend of leaded gasoline uses makes the presence of EDC from gasoline emissions short-lived.

d. Emissions of EDC During Combustion

For the purposes of this materials balance, it is estimated that 1% of the EDC in gasoline is not destroyed during combustion and is released to the atmosphere. This can be calculated as follows:

$$(0.01) \times (9.56 \times 10^4 \text{ kkg}) = 9.6 \times 10^2 \text{ kkg EDC}$$

3.2 RELEASES ASSOCIATED WITH THE MINOR USES OF EDC

In Section 3.1, information is presented which describes the major uses of EDC; these uses accounted for 99.9% of the chemical's annual production. Also described are the environmental releases associated with the listed uses. The purpose of this section is to briefly describe the variety of uses which account for the remaining 0.1% of the annual production of EDC. The emissions associated with these uses will also be discussed.

The minor uses have been grouped as follows (Auerbach Associates, 1978):

- Manufacture of paints, coatings, and adhesives
- Solvent formulations for the extraction of foodstuffs and pharmaceuticals
- Cleaning solvent formulations for PVC reactors and textiles
- Manufacture of polysulfide (rubber cements and elastomers)
- Grain fumigant formulations
- Miscellaneous uses including the manufacture of color film, the processing of copper ores and the formulation of various pesticides and herbicides (used as diluent).

According to the Stanford Research Institute, the minor uses of EDC amounted to 7 kkg in 1974 (Stanford Research Institute, 1975, as cited in U.S. Environmental Protection Agency, 1978a, and also referenced in U.S. Environmental Protection Agency, 1978c). A more recent estimate (for 1977), provided by Auerbach Associates, Inc., indicates that minor uses account for between 4.5 and 5.0 thousand kkg per year (Auerbach Associates, Inc., 1978). The Auerbach Associates estimate is purported to represent the results of a thorough review of the sparse literature references on minor uses of EDC and also numerous direct contacts with industrial facilities involved in the production and use of this chemical. Auerbach Associates concluded that certain solvent uses reported in the literature (and included in the SRI estimates) are either "obsolete or represent an extremely small volume." These uses are as follows: degreasing, fumigation of upholstery and carpets, and additives to soaps and scouring compounds, and as wetting and penetrating agents. The fact that Auerbach Associates did not include the above in their estimate of the total minor uses, plus the difference in base years (1974 vs. 1977), may account for the differences in the estimates of Auerbach and SRI. In view of the fact that the Auerbach Associates estimate represents quite recent direct contacts with industrial concerns involved in the production and use of EDC, it is considered to be the most credible source of available information on minor uses. Table 3.2 is an adaptation from the Auerbach study and presents estimates of the amounts of EDC used in each of six types of use. Based on estimates presented in Section 3.1 and the data in Table 3.2, minor uses account for 0.1% (or 4.8×10^3 kkg) of the annual production of EDC. Uncertainties were not calculated for the above figures because of the insignificant amount of EDC consumed for these uses.

The extent to which EDC emissions are generated as a result of minor uses will vary greatly depending on the use and the manner in which EDC is used within the process. In some processes virtually all EDC used is apparently released to the environment (e.g., grain fumigation). In other processes, the EDC is reacted with other constituents and becomes a bound component of the resulting matrix (e.g., manufacture of polysulfides). Therefore, to adequately assess

TABLE 3.2 MINOR USES OF EDC

Type of Use	Amount (kkg) Range	Amount (kkg) Mean	% of Minor Uses
Paints, Coatings and Adhesives		1364	28
Extraction Solvents	909-1364	1136	23
Cleaning Solvents		909	19
Polysulfides	455-591	523	11
Grain Fumigant		455	9
Miscellaneous Uses		455	9
Total		4842	99%*

*Deviates from 100% due to rounding

the emission potential for the minor uses, it is necessary first to obtain detailed information on how EDC is used in each of these processes. Unfortunately, readily available information sources generally do not provide the detailed descriptions required. Thus, in those cases where there is a paucity of information, there will have to be more reliance on assumptions. In the following paragraphs each of the minor uses will be discussed, and the assumptions needed in order to make emission estimates will be provided.

3.2.1 Releases from EDC Use in the Manufacture of Paints, Coatings, and Adhesives

The uses of EDC in paints, coatings, and adhesives reportedly accounts for over one-fourth of all minor uses. It is assumed that the paints category consists of those paints which use various vinyl polymers as resin. Polyvinyl chloride is one of the polymers used. There are a variety of other protective coatings beside paints (e.g., fabric finishes, leather finishes, and paper coatings) which use vinyl polymers as all or a major part of the coating binder (Connolly, 1977). The use of EDC in adhesives is limited to the acrylic type of compound.

Contact was made with the Paint, Varnish and Lacquer Association in order to determine how EDC is used within this industry. The technical representative contacted indicated he was not familiar with the use of this compound for paints, but that it may be a component of one of the adhesives which utilize "fast" solvents (Brown, 1979). In the absence of data in the literature to the contrary, it is assumed that EDC is used in paints, coatings, and adhesives as a solvent, and that virtually all of the solvent contained in these materials is eventually evaporated to the atmosphere during normal use of these products. A similar assumption was made by the Oak Ridge National Laboratory in a document prepared for EPA (U.S. Environmental Protection Agency, 1978c). In addition to the emissions resulting from the use of paints, coatings, and adhesives containing EDC, other emissions of EDC to the air can be expected to occur during the initial formulation processes at the manufacturing facilities. Based on this assumption, it is estimated that the annual emissions of EDC associated

with the manufacture and use of paints, coatings, and adhesives amount to 1.4×10^3 kkg, which is the total amount of EDC production ascribed to this use.

A Phase II investigation, which involves direct contacts with major manufacturers, should ascertain how EDC is used in the formulation of paints, coatings, and adhesives. If it is verified that EDC becomes a bonded component of coatings of adhesives, it will be necessary to reduce overall emissions estimates by the appropriate amounts.

3.2.2 Releases from EDC Use as an Extraction Solvent

EDC is used in a number of solvent extraction applications. These include the extraction of oil from seeds, the processing of animal fats and the processing of pharmaceutical products. The literature does not provide information on the composition of the solvents used in these extraction procedures, nor are there details describing the processes used. The solvent used in extraction procedures is likely to be recovered via a distillation process (probably involving reduced pressure). Because of the toxicity of EDC, the residual amounts of this substance in the extracted material should be quite small. In 1961, the Federal Food, Drug and Cosmetic Act limited the concentration of EDC in spice oleoresins (for human consumption) to 30 ppm or less, while the residual amounts in processed animal feed in 1967 were limited to 300 ppm (USEPA, 1979a). Thus, little of the EDC is expected to be transferred to the ultimate product of the extraction procedure.

Solvent losses will likely occur during the extraction process. Additional supplies of solvent will have to be added periodically to make up the losses. It is generally assumed that the bulk of these losses will be in evaporation (to the atmosphere) from valves, spills, leaks and during material transfer operations. For the purposes of this materials balance, it is assumed that 95% of the EDC consumed in solvent extraction processes will be lost in this manner. Thus 1.0×10^3 kkg of EDC will be emitted to the atmosphere via this method.

The remaining 5% (60 kkg) is assumed to be associated with the sludge expected to accumulate in the solvent during the extraction process. The sludge will be either disposed of on land or incinerated. In Section 2.1.1.3, it was assumed that 90% of the solid wastes generated were incinerated and the remaining 10% were landfilled. It was further assumed that in each of these processes 5% of the EDC was eventually released to the atmosphere via an assortment of pathways including fugitive emissions, losses during transportation, and incomplete destruction of wastes in the incinerator. Using these same assumptions for the sludges produced as a result of solvent extraction procedures, the following estimates can be made:

.60 kkg = annual amount of EDC associated with sludge generated during solvent extraction procedures

The amount of EDC sent to the incinerator along with the sludge can then be calculated by multiplying the total quantity of EDC associated with the sludge by the estimated percentage designated to be incinerated. In that case,

(60 kkg) (0.90) = 54 kkg

The amount of EDC associated with the sludge sent to landfill can also be estimated by multiplying the total amount of generated sludge by the percentage designated to be landfilled. Therefore

(60 kkg) (0.1) = 6 kkg

The quantity of EDC released to the air from the incinerator can also be calculated by multiplying the quantity of EDC associated with the incinerated sludge by the inefficiency factor of the incinerator. In that case,

(54 kkg) (0.05) = 2.7 kkg

More information needs to be obtained (most likely via direct contacts with oil and pharmaceutical manufacturers and fat processors) concerning extraction practices involving EDC. Such data could be obtained during a Phase II investigation and would provide a basis upon which to evaluate the validity of assumptions made.

3.2.3 Releases from EDC Use in Cleaning Solvents

Solvents containing EDC are typically used for cleaning processes within the PVC and textile manufacturing industries. The available literature does not provide information on the composition of these solvents, nor on the characteristics of the cleaning operations. Based on the general nature of solvent-based cleaning processes, one would expect virtually all the solvents used ultimately to be evaporated from the surface of the substrate being cleaned (as opposed to being chemically or otherwise permanently incorporated into the substrate). These evaporation losses represent releases to the atmosphere. Lost solvent will be replaced with make-up, and it is assumed that the EDC content of the make-up added accounts for most (95%) of the 9.1×10^2 kkg of EDC consumed and assumed lost to the atmosphere during solvent cleaning processes. Therefore, the quantity of EDC released to the atmosphere during the solvent cleaning operations can be calculated as follows:

$$(0.95) \times (9.1 \times 10^2 \text{ kkg}) = 864 \text{ kkg} = \text{EDC}$$

Solids and dense materials removed during the cleaning process will accumulate in the solvent, and will thereby generate a sludge waste stream. It is assumed the EDC associated with this sludge will account for the remaining 5% of the EDC consumed during solvent cleaning operations. Therefore,

$$(0.05) \times (9.1 \times 10^2 \text{ kkg}) = 46 \text{ kkg} = \text{Amount of EDC Associated with the Sludge Generated During Solvent Cleaning Operations}$$

The sludge will likely be removed during solvent recovery operations and will be disposed of either by landfilling or incineration.

Using the same assumptions developed for the sludges produced from

solvent extraction processes, the following estimates can be made:

The amount of EDC associated with the sludge sent to the incinerator can be calculated by multiplying the total quantity of EDC present in the sludge by a factor of 0.9. In this case,

$$(0.9)\ (46\ \text{kkg}) = 41\ \text{kkg}$$

The amount of EDC present in the sludge sent to landfill can then be calculated by multiplying the total quantity of EDC in sludge by the factor 0.1. Therefore:

$$(0.1)\ (46\ \text{kkg}) = 4.6\ \text{kkg}$$

The amount of EDC ultimately released to the atmosphere during sludge incineration can also be calculated by multiplying the amount of EDC in sludge sent to the incinerator by the inefficiency factor of the incinerator. This amounts to:

$$(0.05)\ (41\ \text{kkg}) = 2\ \text{kkg}$$

3.2.4 Releases of EDC Associated with the Manufacture and Use of Polysulfides

Polysulfides are a group of rubber-like polymers which are obtained via the reaction between aliphatic dihalides and alkali polysulfides (Hienisch, 1974; Considine, 1974). The basic formula for the reaction between EDC and Na_2S_4 is given below (Considine, 1974):

$$n(\text{EDC}) + n\text{Na}_2\text{S}_4 \longrightarrow (\text{CH}_2\text{CH}_2\text{-S}_4)_n + 2_n\text{NaCl}$$

After final processing, the resulting polymer has excellent resistance to solvents (aliphatic and aromatic), oxidation, ozone, the effects of weather, water and temperatures as low as $-50^{\circ}C$ (Hienisch, 1974).

Based on the chemistry of the reaction and the properties of resulting polymer, it seems reasonable to assume that most of the EDC used during the manufacturing of polysulfides ends up as a component of the end product. For the purpose of this report, we are assuming this amounts to 94%; this estimate is based on the typical industrial chemical reactions and yields. Since the portion of the total

production of EDC consumed for the manufacture of polysulfides is 5.2×10^2 kkg, 4.9×10^2 kkg is assumed to be chemically incorporated in the polysulfide product.

$$(0.94) \times (5.2 \times 10^2 \text{ kkg}) = 489 \text{ kkg} = 4.9 \times 10^2 \text{ kkg}$$

It is generally assumed that an additional 5% (or 26 kkg) of the EDC consumed in this process will be released to the atmosphere via leaks, spills and fugitive emissions associated with the overall polysulfide manufacturing process.

$$0.05 \times 5.2 \times 10^2 \text{ kkg} = 26 \text{ kkg}$$

The initial production reaction is typically performed in an alkaline aqueous phase; therefore, some of the unreacted EDC may dissolve in the reaction mixture. Available data indicates that EDC is only slightly soluble (1%) in distilled water (Weast, 1977; Windholtz, 1976). Thus, one would not expect more than 1% of the EDC to be dissolved, in the mother liquor, as an unreacted species. It is possible that reaction conditions (alkalinity, temperature, etc.) may induce hydrolysis of some of the EDC present in the reaction mixture before it has had a chance to react with the alkali polysulfide. It should be noted that if this were to occur, it would still represent the chemical incorporation of EDC into relatively stable compounds. But since the desired product of the reaction is the polysulfide, it is reasonable to expect the reaction conditions to be adjusted to discourage the production of unwanted by-products. In spite of the above, it seemed reasonable to assume that 1% of the EDC used for polysulfide manufacture remains as a dissolved constituent in the mother liquor from which the polymer is produced. Therefore, the amount of EDC remaining in the mother liquor can be calculated by multiplying the total amount of EDC consumed for the manufacturing of polysulfide by the estimated factor. In this case,

$$(0.01) \ (5.2 \times 10^2 \text{ kkg}) = 5.2 \text{ kkg}$$

The fate of the mother liquor is not known, but for the purposes of this materials balance, the mother liquor is assumed to be discharged

as solid waste and stored in landfills.

3.2.5 Releases from EDC Use in Grain Fumigation

There are a variety of grain fumigant formulations for which EDC is a constituent. The composition of some of the fumigants manufactured by Dow are presented in Table 3.3 (Gosselin, et al., 1976). As shown in Table 3.3, the grain fumigants manufactured by Dow are generally various mixtures of EDC, dibromoethane and carbon tetrachloride. The composition of fumigants produced by other manufacturers may differ, but some of the formulations also contain EDC (Stanford Research Institute, 1976).

The process of grain fumigation involves exposing grain to fumigant vapors under specified conditions of time, temperature, etc., and then allowing for ventilation of the exposed grain. It is unlikely that attempts will be made to collect the exhaust gases during ventilation; therefore, it is reasonable to assume that all fumigant vapors which are not retained by the grain will be released to the atmosphere. The amount of fumigant retained by the grain depends on a variety of factors including type of grain, extent of grinding, type and concentration of fumigant applied, general exposure conditions, and length and nature of subsequent ventilation (U.S. Environmental Protection Agency), 1978c). It appears that the retention of EDC is due to both chemical and physical processes, but investigators differ widely on the total quantity of the chlorinated hydrocarbon which remains absorbed. Even though some investigators have reported very high (84%) sorption efficiencies for certain cereal substrates (Berck, 1965), the generally accepted conclusions are that by the time the grain is processed and ready to be consumed, essentially all of the retained EDC will have been dissipated to the atmosphere (U.S. Environmental Protection Agency, 1978c). For this reason, it is assumed that 100% of the EDC used for grain fumigation (totaling 4.6×10^2 kkg) is eventually released to the atmosphere.

TABLE 3.3 COMPOSITION OF SELECTED FUMIGANTS*

Trade Name	Composition (%)		
	1,2 Dichloroethane	Carbon Tetrachloride	1,2-Dibromoethane
Dowfume 75	70	30	-
Dowfume EB-5	29	64	7
Dowfume EB-15 Inhibited	20	57	20
Dowfume EB-59	9	32	59
Dowfume J	63.5	29.7	7.8
Dowfume V	15	83	2

*Table represents only those fumigants manufactured by Dow

Source: Adapted from SRI, 1975

3.2.6 Releases from Other Uses

Three miscellaneous uses of EDC include (1) the manufacture of color film, (2) a diluent for pesticides and herbicides, and (3) an amine carrier during the leaching of copper ores. Here again, there is a paucity of information in the readily available literature regarding the details of the processes associated with these miscellaneous uses. Therefore, it was assumed that the 4.6×10^2 kkg of EDC consumed for this purpose was equally divided among the three identified uses. It was further assumed that all of the EDC used in the color film and pesticide/herbicide industry was eventually released to the atmosphere, but that used for copper processing was chemically incorporated with amines and other materials involved in the copper leaching process. Thus, 66% of the 4.6×10^2 kkg of EDC used for miscellaneous purposes is assumed to be released directly to the atmosphere, while the remaining 34% is assumed to be chemically incorporated into materials associated with the copper leaching process.

The amount of EDC used for miscellaneous purposes can then be calculated by multiplying the quantity of EDC used in this category (4.6×10^2 kkg) by the estimated percentage. Therefore:

$$(4.6 \times 10^2 \text{ kkg}) \ (0.66) = 3.0 \times 10^2 \text{ kkg}$$

The remaining quantity of EDC used in copper leaching process can also be calculated by multiplying the quantity used in this category by the remaining percentage. In this case,

$$(4.6 \times 10^2 \text{ kkg}) \ (0.34) = 1.6 \times 10^2 \text{ kkg}$$

4.0 SUMMARY OF POINTS OF ENVIRONMENTAL RELEASE

The environmental releases of EDC during its production, distribution, and use are estimated to have been 65,000 kkg in 1977. This section highlights the releases that are of importance in terms of quantity and location of release. Releases, the point-sources of release and the geographic location of the producers and users of EDC are shown in Section 2 and 3.

The two largest sources of release, each representing 30% of the total quantity of EDC released, are the quantities of EDC released to the air during the direct chlorination and the oxychlorination processes for producing EDC. The quantity of EDC released from process vents and light-end streams of each production process amounts to approximately twenty thousand kkg. Most of the plants producing EDC use both of these processes. Therefore, a total of seventeen plants producing EDC release close to 60% of the total EDC released to the environment and this release is to the atmosphere. Most of these production facilities are located in the Gulf Coast regions of Louisiana and Texas.

Monitoring data have indicated that EDC is present in the ambient air near production facilities. It has been theorized from these data that the EDC emissions from a stack drop to the ground level and, depending on local climatological and topographic factors, they tend to follow valleys and low-lying areas (EPA, 1978d). This theory is dependent on and consistent with the vapor density of EDC which is 3.42, given the density of air = 1. It is important to note here that, according to the American Public Health Association statistics (1975), 1,379,000 people live within 5 miles of an EDC manufacturing facility.

The next two largest sources of emissions are those in wastewater streams from both production processes for EDC. These quantities are 4,900 kkg (or 8% of the total) from the wastewater stream of the oxychlorination process and 4,400 kkg (7% of the total) from the wastewater stream of the direct chlorination process.

Other potentially important releases (each 1% of the total) of EDC include the following:

- Methyl chloroform production process vents (2.3%)
- Paints, coatings, and adhesives formulation (2.0%)
- Gasoline lead scavenger (1.6%)
- Extraction solvent (1.4%)
- Perchloroethylene production process vents (1.3%)
- Cleaning solvent (1.2%)

It is important to note that regulation promulgated by the authority of the Occupational Safety and Health Act restricts the quantities of EDC released in the workplace. The only workplace environment where EDC releases are not fully regulated is the gas station. It is not possible to adequately measure worker exposure at gas stations since ambient air levels are not representative of worker exposure.

5.0 SUMMARY OF DISPOSAL AND DESTRUCTION OF SOLID AND LIQUID EDC-CONTAINING WASTES

This chapter summarizes the information on the quantities of EDC-containing solid and liquid wastes destroyed and disposed of during the production and uses of EDC. According to Gruber (1975), incineration was apparently the only method of disposing of EDC-containing wastes.

As shown in Table 5.1, the amounts of EDC present in heavy-end waste streams of the direct chlorination process, the oxychlorination process and the vinyl chloride monomer production process are 2.2×10^3 kkg, 3.1×10^3 kkg, and 2.0×10^3 kkg respectively. Assuming that the incinerator used in the destruction of heavy-end waste achieves a 95% efficiency, the quantity of EDC destroyed from the above heavy-end wastes is, respectively, 2.1×10^3 kkg, 2.9×10^3 kkg, and 1.9×10^3 kkg. The uncertainty of these figures is unknown because of the lack of information.

The quantity of EDC present in the sludge generated from the use of EDC as a solvent for paints, coating and cleaning purposes is estimated at 100 kkg. The sludge is assumed to be incinerated and the quantity of EDC destroyed amounts to 95 kkg. The remaining 5 kkg is released intact to the air. The uncertainty of this figure is not calculated.

TABLE 5.1 - SOLID AND LIQUID EDC-CONTAINING WASTE QUANTITIES, DISPOSAL, AND ENVIRONMENTAL RELEASE

TYPE OF WASTE PRODUCED	AMOUNT OF EDC PRESENT IN SLUDGE GENERATED FROM WASTEWATER TREATMENT (kkg)	AMOUNT OF SOLID WASTE (kkg)	QUANTITY DESTROYED BY INCINERATION (kkg)	QUANTITY RELEASED TO AIR FROM INCINERATION (kkg)
-- Direct chlorination of ethylene				
• Heavy-end waste		2.2×10^3	2.1×10^3	1.1×10^2
-- Oxychlorination of ethylene				
• Heavy-end waste		3.1×10^3	2.9×10^3	1.6×10^2
-- Vinyl chloride monomer production process				
• Heavy-end waste		2.0×10^3	1.9×10^3	1.0×10^2
• Solvent for paint and coating	60		54	6
• Cleaning solvent	46		41	5

6.0 SUMMARY OF UNCERTAINTIES

Table 6.1 lists the estimates for environmental releases and the associated uncertainties of EDC by process and by media of release. The rationale for assigning a specific uncertainty to each number is discussed in Chapters 2 and 3. Our recommendations for upgrading the material balance are presented in Chapter 7.

TABLE 6.1 SUMMARY OF UNCERTAINTIES FOR ESTIMATES OF ENVIRONMENTAL RELEASE FROM PRODUCTION AND USE OF EDC

Process/Operation	Method of Environmental Release	Quantity (kkg)	Uncertainty
The direct chlorination process	TOTAL PRODUCTION	2.94×10^6	±1%
	EMISSION TO AIR		
	- Chlorinator vent		
	a - uncontrolled	2.9×10^3	+150%, -95%
	b - controlled	58	+53%, -100%
	- Light-End column vent		
	a - uncontrolled	3.0×10^3	+150%, -96%
	b - controlled	3.0×10^2	+280%, -97%
	- EDC distillation column vent		
	a - uncontrolled	3.0×10^3	+200%, -96%
	b - controlled	3.0×10^2	+350%, -97%
	- Product storage		
	a - uncontrolled	1.1×10^4	±44%
	b - controlled	5.3×10^2	+200%, -79%
	- Fugitive losses		
	a - uncontrolled	1.8×10^2	+150%, -96%
	b - controlled	18	+340%, -100%
	- Wastewater treatment	4.4×10^3	+150%, -96%
	- Heavy-End waste incineration	1.1×10^2	+250%, -98%
The oxychlorination process	TOTAL PRODUCTION	2.05×10^6	±1%
	EMISSION TO AIR		
	- Absorber vent		
	a - uncontrolled	2.1×10^3	±96%
	b - controlled	2.1×10^2	+190%, -97%
	- EDC stripper vent		
	a - uncontrolled	5.6×10^3	±96%
	b - controlled	1.1×10^2	+500%, -100%
	- Light-End column vent		
	a - uncontrolled	2.1×10^3	±96%
	b - controlled	2.1×10^2	+190%, -97%
	- EDC distillation column vent		
	a - uncontrolled	2.1×10^3	±96%
	b - controlled	2.1×10^2	+190%, -97%
	- Product storage		
	a - uncontrolled	7.6×10^3	±44%
	b - controlled	3.8×10^2	+200%, -80%

TABLE 6.1 SUMMARY OF UNCERTAINTIES FOR ESTIMATES OF ENVIRONMENTAL RELEASE FROM PRODUCTION AND USE OF EDC (cont.)

Process/Operation	Method of Environmental Release	Quantity (kkg)	Uncertainty
	- Fugitive emission		
	a - uncontrolled	1.3×10^2	±96%
	b - controlled	13	+310%, -100%
	- Wastewater treatment	4.9×10^3	±96%
	- Heavy-end waste incineration	1.6×10^2	+150%, -98%
Indirect Production	EMISSION TO WATER		
	- Quantity of POTW/year	8.2×10^{12} gal	±25%
	- Amount of EDC released	2.2	+150%, -100%
	- Quantity of industrial wastewater treated/year	1.6×10^{13} gal	±25%
	- Amount of EDC released	1.9×10^2	+150%, -100%
	- Amount of EDC formed by incinerating MSW	0.06 - 0.3	±70%
	- Amount of EDC formed from other inadvertent sources	5×10^{-4}	+200%, -100%
Vinyl chloride monomer production	TOTAL PRODUCTION (from EDC)	2.48×10^6	±1%
	- Amount of EDC used	4.05×10^6	±2%
	- Emission of EDC to land	2.0×10^3	±51%
	- Emission of EDC to air (incineration)	99	+110%, -70%
Trichloroethylene production	TOTAL PRODUCTION (from EDC)	1.2×10^5	±1%
	- Amount of EDC used	1×10^3	±2%
	- Emission of EDC to air	610	±51%
Perchloroethylene (from EDC)	TOTAL PRODUCTION (from EDC)	2.8×10^5	±1%
	- Amount of EDC used	1.2×10^5	±2%
	- Emission of EDC to air	910	±51%
Perchloroethylene (from acetylene)	- Emission of EDC to air	20	±51%
Vinylidine chloride production	TOTAL PRODUCTION (from EDC)	1×10^5	±1%
	- Amount of EDC used	1.2×10^5	±3%
	- Emission of EDC to air	600	±51%

TABLE 6.1 SUMMARY OF UNCERTAINTIES FOR ESTIMATES OF ENVIRONMENTAL RELEASE FROM PRODUCTION AND USE OF EDC (cont.)

Process/Operation	Method of Environmental Release	Quantity (kkg)	Uncertainty
Methyl chloroform production	TOTAL PRODUCTION (from EDC)	2.6×10^5	±1%
	- Amount of EDC used	2.1×10^5	±3%
	- Emission of EDC to air	1.6×10^3	±51%
Ethyleneamines	TOTAL PRODUCTION (from EDC)	6.9×10^4	±5%
	- Amount of EDC used	1.5×10^3	±10%
	- Emission of EDC to air	610	±51%
Lead scavenger production	EDC USED	9.7×10^4	±100%
	- Emission of EDC to the air during production of leaded gasoline	97	unknown
	- Emission of EDC to the air from tank breathing	11	unknown
	- Emission of EDC to the air from tank filling		
	a - uncontrolled	84	unknown
	b - controlled	67	unknown
	- Emission of EDC to the air from combustion	9.6×10^2	unknown

7.0 DATA GAPS

During the preparation of this report, a series of significant data gaps were identified. This section lists and discusses these gaps in information. In many cases, suggestions are made for methods that could be utilized to obtain the needed information. Most important, this section pinpoints areas where additional research is necessary.

7.1 DATA NECESSARY TO INCREASE THE VALIDITY OF EMISSIONS ESTIMATED FOR VARIOUS PRODUCTION PROCESSES

The estimate of emissions for many of the major production processes were based primarily on one reference (Hedley et al., 1975). Review of this source indicates that no substantiating information was provided. While the Hedley figures do not seem unreasonable, it is clear that in its present unsubstantiated and unexplained form, this report does introduce an element of uncertainty. Additional supporting information should be obtained by contacting Hedley or individuals in the manufacturing industry.

7.2 ESTIMATES OF THE OCCURRENCE AND RELEASE OF EDC AS A BY-PRODUCT OF MANUFACTURING PROCESSES FOR WHICH EDC IS NOT A FEEDSTOCK

Production processes which use synthetic organic chemical reactions could generate EDC as a by-product along with the major desired product. If produced, such a by-product stream could (1) be recovered and sold, (2) become a contaminant of the major product or (3) become a component of some waste stream. Since this by-product generation could occur in a manufacturing area unrelated to those described in this report, any potential emissions of EDC from such a source would not be accounted for in this analysis. Therefore, any significant emissions of EDC which have been

generated as a by-product could have a substantial effect on the overall materials balance as represented in this report.

In Section 2 of this report, these possibilities are analyzed, and very rough estimates are made. In addition, the Effluent Guidelines Division of EPA has indicated that EDC as a priority pollutant is present in the wastewater of many industries. This area must be explored further.

7.3 DETERMINING EMISSION LEVELS OF EDC ASSOCIATED WITH CERTAIN MAJOR USES

As pointed out in Section 3.1 of this report, information on EDC emissions to various segments of the environment is very limited for production processes using EDC as a feedstock. These processes include the following: production of vinyl chloride, trichloroethylene, perchloroethylene, ethyleneamines and vinylidine chloride. Thus, it is very difficult to properly assess the emission of EDC during the production of the above chemicals. Further studies should be conducted to expand the data base.

Analyses obtained from monitoring data on wastewater streams discharged by the chemical producers mentioned above do not identify EDC as a component of the waste stream. It is suggested that EDC contamination could occur in the wastewater stream and EDC could rapidly evaporate to the air (due to its high volatility) before the waste treatment cycle. Therefore, this potential source of EDC release to the atmosphere should be investigated in further studies.

Likewise, information on EDC emission from solid waste such as the heavy-end tars stream is not available for most of the production processes (vinylidene chloride, trichloroethylene, perchloroethylene, and ethyleneamines). Possible release of EDC to the environment from this source could be significant; therefore, it deserves more in-depth study in further investigations.

7.4 DATA GAPS RELATING TO MINOR USES OF EDC

As described in Section 3.2, there is limited information concerning minor uses of EDC and the associated emissions. Specific data gaps are presented below:

- Information on the nature of minor uses of EDC (e.g., whether EDC is used as a solvent or a bound constituent in paints, coatings and adhesives; whether there are vapor recovery systems for grain fumination; etc.)
- Composition of cleaning and extraction solvents which contain EDC
- Accurate assessment of the amount and nature of EDC use (1) in the manufacture of color film; (2) as a herbicide and pesticide diluent; and (3) in copper leaching processes.

Many of the data gaps concerning minor uses will have to be closed via direct contacts with manufacturing concerns, since most of the required information is not present in the available literature.

7.5 EDC PRODUCTION DURING THE CHLORINATION OF WATER AND WASTEWATER

The National Organic Monitoring Survey (NOMS) revealed the presence of EDC at low levels (EPA, 1978) in both raw and finished water. It was suggested that EDC is formed by the reaction of organic impurities present in water with chlorine added at the water treatment plant. Another possible explanation for this occurrence of EDC in municipal water is that the raw water effluent is taken near a point source of EDC emissions. The NOMS data for these municipal systems should be examined to verify any conclusions. In addition, the formation of EDC as a result of wastewater chlorination requires further study.

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7.6 EDC PRODUCTION FROM INCINERATION OF CHLORINATED ORGANIC COMPOUNDS

Although estimates were made for the release of EDC as a result of the incineration of chlorinated organics, many assumptions were used as the basis for these estimates. Virtually no hard data was retrieved which indicated that EDC could in fact be produced through the incineration of chlorinated organic compounds. Further research in the behavior of these compounds must be conducted before accurate assessments can be made.

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APPENDIX A

PHYSICAL PROPERTIES OF

1,2-DICHLOROETHANE

Physical Properties of 1,2-Dichloroethane

Molecular weight	98.96
Density at 20°C	1.2351
Melting point, °C	-35.36
Boiling point, °C	83.47
Index of refraction at 20°C	1.4448
Vapor pressure, torr	
At -44.5°C	1
At -13.6°C	10
At 10.0°C	40
At 29.4°C	100
At 64.0°C	400
At 82.4°C	760
Solubility in water, ppm	
At 20°C	8690
At 30°C	9200
Biochemical oxygen demand (5 days), %	0
Theoretical oxygen demand, mg/mg	0.97
Measured chemical oxygen demand, mg/mg	1.025
Vapor density (air = 1)	3.42
Flash point, closed cup, °C	13
Ignition temperature, °C	413
Explosive limit, % by volume in air	
Lower	6.2
Upper	15.9
Specific resistivity	9.0×10^{6}
Viscosity at 20°C, cP	0.840
Dielectric constant, ϵ	10.45
Surface tension, dynes/cm	33.23
Coefficient of cubical expansion at 10°C to 30°C	0.0016
Latent heat of fusion, cal/g	21.12
Latent heat of vaporization at boiling point, cal/g	77.3
Specific heat, cal g^{-1} $°C^{-1}$	
Liquid at 20°C	0.308
Vapor, 1 atm, at 97.1°C	0.255
Critical temperature, °C	288
Critical pressure, atm	53
Critical density, g/cm^3	0.44
Thermal conductivity at 20°C, Btu hr^{-1} ft^{-2}	0.825
Heat of combustion at constant pressure, kcal/g-mole	296.36
Dipole moment, esu	1.57×10^{-18}
Conversion factors at 25°C and 760 torr	1 mg/liter = 1 g/m^3 = 247 ppm 1 ppm = 4.05 mg/m^3 = 4.05 µg/liter

Source: Compiled from Faith, Keyes, and Clark, 1965a; Price, Waggy, and Conway, 1974; Verschueren, 1977; Weast, 1977.

APPENDIX B

EXCERPTED DESCRIPTIONS OF MAJOR PROCESSES WHICH PRODUCE OR USE EDC

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Various information on the 1,2-dichloroethane chemical intermediate production processes are included in this appendix. This information is excerpted from the following sources:

1. Gruber, G. I., Ghassemi, M., 1975. Assessment of Industrial Hazardous Waste Practices: Organic Chemicals, Pesticides, and Explosives Industries. EPA Contract No. 68-01-2919.

2. U. S. Environmental Protection Agency, 1979. An Assessment of the Need for Limitations on Trichloroethylene, Methyl Chloroform, and Perchloroethylene. EPA 560/11-79-009, Washington, D. C.

3. U. S. Environmental Protection Agency, 1978. Air Pollution Assessment of Vinylidene Chloride. EPA 450/3-78-015, Washington, D. C.

4. Lowenheim, F. H., and M. K. Moran, 1975. "Ethylene Diamine" In: Faith, Keyes, and Clark's Industrial Chemicals, 4th edition. John Wiley & Sons, New York. pp. 385-388.

5. McPherson, R. W., Starks, C. M., Fryar, G. J., "Vinyl Chloride Monomer". Hydrocarbon Processing, 58, 3, 1979.

B.1 Vinyl Chloride Monomer SIC 28692[016,308,310,341] (Source: Gruber 1975)

The production rates in 1973 for vinyl chloride monomer (VCM) and for ethylene dichloride (EDC), the intermediate used in the majority of manufacturing processes were 2,432,000 metric tons (5,351 million pounds) and 4,215,000 metric tons (9,293 million pounds)[030]. There were ten major producers reported:[068] Allied Chemical Corporation (Specialty Chemicals Division), American Chemical Company, B. F. Goodrich Company (B. F. Goodrich Chemical Company Division), Continental Oil Company, Dow Chemical Company, Tenneco Chemicals Incorporated, Monochem Incorporated, Pittsburgh Plate Glass Company, Shell Oil Company (Shell Chemicals Company Division) and Ethyl Corporation. A typical plant size is 136,000 metric tons per year, with plant capacities which range from 27,000 metric tons to 317,500 metric tons per year for the major process system employed.[310]

The process flow diagram of Figure 5-14 is a composite typical department for the production of vinyl chloride from ethylene and chlorine. Ethylene dichloride is produced continuously by the liquid phase catalyzed addition chlorination reaction between ethylene and chlorine, fed as gaseous reactants to a pressurized vessel. The reaction which takes place is:

$$H_2C = CH_2 + Cl_2 \xrightarrow[T\ 370°K]{FeCl_3} ClH_2C\text{-}CH_2CL \text{ (EDC)}$$

The catalyst employed is ferric chloride, suspended in liquid ethylene dichloride. The product ethylene dichloride is liquified, scrubbed with dilute caustic soda solution, filtered and distilled. The heavy ends from the still (0.0104 kg per kg product VCM) are a hazardous process waste, sent to land disposal. The heavy ends contain highly dangerous components--ethylene dichloride (23 percent), 1,1,2-trichloroethane (38 percent) and tetrachloroethane (38 percent)--which are bioaccumulable.

The purified EDC from the still is fed to the pyrolysis furnace for the production of vinyl chloride monomer, in accordance with the following reaction:

$$ClCH_2CH_2Cl \xrightarrow[750\text{-}780°K]{\text{Catalyst}} HCl + CH_2 = CH_2Cl \quad \text{(VCM)}$$

The reaction takes place in the vapor phase, at 450-620 x 103 newtons/meter^2 (50-75 psig). The catalysts employed may be activated carbon or pumice. When

mercuric chloride is employed as catalyst, lower temperatures (720°K) and higher pressures (520-930 x 10^3 newtons/meter^2) are used. Conversion per pass is 50 percent; with recycle, the pyrolysis yield is 95 to 96 percent.

The product gas stream from the furnace, containing VCM, EDC and HCl is quenched with recycled liquid EDC, and condensed. The hydrogen chloride is separated in the condenser, since it remains (as the sole constituent) in the gas phase, and is sent to recovery, or to use in an oxy-chlorination unit for the production of EDC by reaction with ethylene.

The liquid effluent from the condenser is sent to a still, where it is separated into VCM product, recycle EDC, and "heavy ends" (about 0.038 kg/kg VCM product). The "heavy ends" are a hazardous process waste sent to land disposal. They are in this case composed of higher halogenated hydrocarbons (97 percent), EDC (2 percent) and tars (1 percent), and are considered highly dangerous. When mercuric chloride is used as catalyst, there is also a discharge of mercuric "hydroxide" (hydrated oxide) to land in the filter solids, estimated at 5 x 10^{-6} kg/kg VCM.

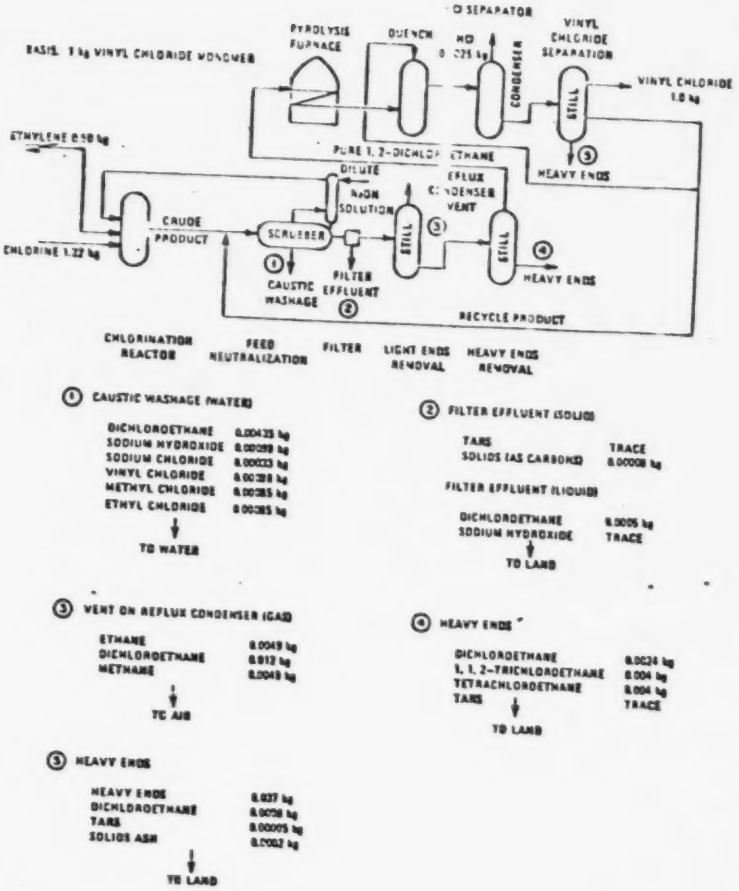


Figure B-1. Typical Production Process for Vinyl Chloride Monomer from 1,2-Dichloroethane
(Source: Gruber, 1975)

B.3 Perchloroethylene Production Technology (Source: EPA, 1979)

In 1975 nearly all of the perchloroethylene output in the United States was derived from the oxychlorination of ethylene dichloride (about 34% of output), or by the simultaneous chlorination and pyrolysis of hydrocarbons (about 63% of output). Approximately 3% was based on the use of acetylene as a raw material (Lowenheim and Moran, 1975).

B.3.1 Production From Ethylene Dichloride--

The typical process for manufacture of perchloroethylene and trichloroethylene from ethylene dichloride was shown in Figure 3-6 and the process described in Subsection 3.1.3.

B.3.2 Production from Acetylene (Source: Gruber, 1975)

Production of perchloroethylene ("tetrachloroethylene") in 1973 totalled 320,000 metric tons (706 million pounds). There were eight major producers--Diamond Shamrock Corporation, Dow Chemical Company, and E. I. duPont de Nemours and Company, Inc., Vulcan Materials Company (Chemical Division), Hooker Chemical Corporation (Division of Occidental Petroleum), Pittsburgh Plate Glass Company, Stauffer Chemical Company (Industrial Division), and Ethyl Corporation. Typical plant sizes are in the range of 32,000 to 45,000 metric tons (50 to 100 million pounds) per year.

About 20% of the perchloroethylene manufactured uses chlorine and acetylene as starting materials. The chemistry of the reactions is as follows:

$$2\,Cl_2 + HC \equiv CH \xrightarrow[80°C]{SbCl_3} C_2H_2Cl_4$$

$$C_2H_2Cl_4 \xrightarrow[300°C]{Catalyst} Cl\text{-}CH = CCl_2 + HCl$$

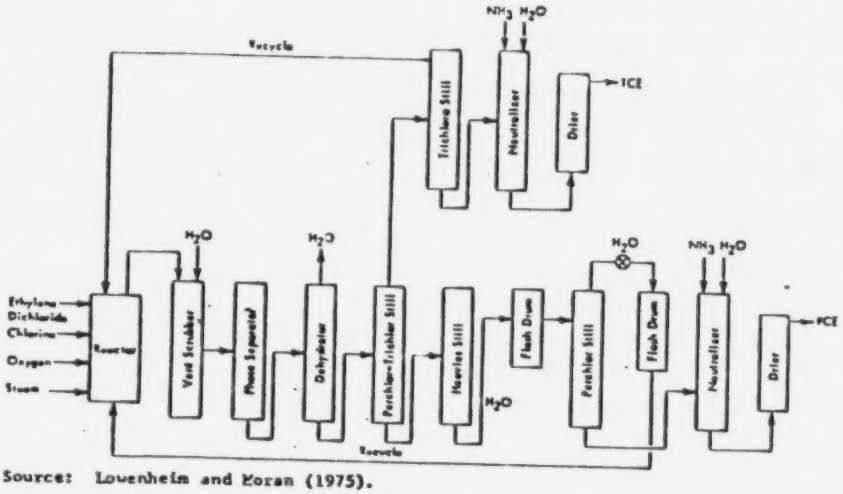
$$ClCH = CCl_2 + Cl_2 \xrightarrow[70\text{-}80°C]{FeCl_3} Cl_2CHCCl_3$$

$$2Cl_2CHCCl_3 + Ca(OH)_2 \xrightarrow{80°C} Cl_2C = CCl_2 + CaCl_2 + 2H_2O$$

Chlorine and acetylene, each individually premixed with a reaction medium of recycled tetrachloroethane and antimony trichloride catalyst, are fed to a packed chlorination tower. The reaction product (see Figure B-3) is fed to a still and separated into spent antimony chloride catalyst, tetrachloroethane,

The crude trichloroethylene stream is fed into a product still in which low boiling components, such as dichloroethylenes, are removed as an overhead stream and recycled to the reactor. The purified product (99.9+ wt % purity) is removed from the bottom of the still, neutralized with ammonia, washed, and dried. The overall yield of trichloroethylene in this process is 85 to 90%.

By-products and wastes from this process are hydrogen chloride (recovered as hydrochloric acid); chlorine (produced from hydrogen chloride by the Deacon process using a copper chloride catalyst); and atmospheric (water vapor) emissions from the crude product dehydrator unit (Lowenheim and Moran, 1975).



Source: Lowenheim and Moran (1975).

Figure B-2. Production schematic for trichloroethylene based on ethylene dichloride.

Source: EPA, 1979

B.2 Trichloroethylene Production Technology

In 1975, about 90% of the commercial production of trichloroethylene was by the chlorination or oxyhydrochlorination of ethylene to form the intermediate ethylene dichloride, which was in turn chlorinated and then dehydrochlorinated to form trichloroethylene. The remaining 10% was still manufactured by an older process which involves chlorination of acetylene in the presence of a catalyst, followed by dehydrochlorination of the 1,1,2,2-tetrachloroethane intermediate.

B.2.1 Production From Ethylene Dichloride--

A typical process for the manufacture of trichloroethylene and perchloroethylene from ethylene dichloride is shown in Figure B-2. There are several other commercial processes based on ethylene dichloride.

Trichloroethylene and perchloroethylene are produced as co-products in a single-stage oxychlorination process from ethylene dichloride and chlorine. As market demands dictate, the product ratios can be varied from nearly 100% trichloroethylene to 100% perchloroethylene by adjusting the proportions of raw materials and process conditions (Lowenheim and Moran, 1975).

The principal reactions in this process are:

$$2C_2H_4Cl_2 + 5Cl_2 \longrightarrow C_2H_2Cl_4 + C_2HCl_5 + 5HCl$$

$$C_2H_2Cl_4 + C_2HCl_5 \longrightarrow C_2HCl_3 + 2HCl + C_2Cl_4$$

$$7HCl + 1.75O_2 \longrightarrow 3.5H_2O + 3.5Cl_2 \text{ (Deacon)}$$

$$2C_2H_4Cl_2 + 1.5Cl_2 + 1.75O_2 \longrightarrow C_2HCl_3 + C_2Cl_4 + 3.5H_2O$$

Based on a final production of 1 kg of perchloroethylene and 0.793 kg of trichloroethylene, the quantities of raw materials are 1.195 kg of ethylene dichloride, 0.642 kg of chlorine, 0.388 kg of oxygen, and a small quantity of oxychlorination catalyst (Lowenheim and Moran, 1975).

Ethylene dichloride, recycled chlorinated organics, chlorine, and oxygen are charged to a fluid bed reactor which is maintained under pressure and at a temperature of about 425°C. The reaction product, containing trichloroethylene, perchloroethylene, and hydrogen chloride, is passed through a vent scrubber.

After vent scrubbing of the product gas stream with water, the weak hydrochloric acid and the condensed crude product are phase separated. Azeotropic distillation is used to dry the crude; the overhead stream from this dehydration step is vented to the atmosphere. The dehydrated crude is fed to a perchlor-trichlor still column in which the crude is split into two streams, one rich in trichloroethylene and the other rich in perchloroethylene.

and vent gas. The spent antimony trichloride catalyst is sent to recovery; overall catalyst loss is small[351], and estimated as 1kg/1 million kg product.

The tetrachloroethane is split into a recycle stream, and a dehydrochlorinator feed stream. The dehydrochlorination of the tetrachloroethane takes place in a packed tower, filled with activated carbon catalyst, at 573°K (300°C). The reaction products, trichloroethylene and hydrogen chloride are cooled and the liquid and gas phases separated. The gaseous phase hydrogen chloride is absorbed in water, and sold as commercial grade muriatic acid.

The condensate trichloroethylene is fed to a degasser and then to a still for purification. The tails from the purification column constitute a "heavy ends" process waste stream. The combined heavy ends from this purification column and the perchloroethylene purification column are approximately 0.30 kg per kg product; they are sent to land disposal.

The purified trichloroethylene is fed to a chlorination tower where chlorination to pentachloroethane takes place at 343-353°K (70-80°C) in the presence of a ferric chloride catalyst. The product pentachloroethane is dehydrochlorinated, using aqueous slaked lime suspension, in a heated packed tower maintained at 80°C. The aqueous phase, containing unreacted slaked lime, calcium chloride and trace quantities of chlorinated solvents, is discharged after separation from the perchloroethane through an industrial outfall.

The crude perchloroethylene after phase separation, is fed to a purification column. Product refined "perc" (perchloroethylene) is sent to storage. The column bottoms, or "heavy ends" are sent to land disposal. As noted earlier, the combined heavy ends from the trichloroethylene and perchloroethylene columns are about 0.30 kg per kg perchloroethylene product; analysis is about 77% hexachlorobutadiene, 7% chlorobenzenes, 7% tars and residues, 3% chloroethanes, and 3% chlorobutadienes. These heavy ends constitute a hazardous waste stream to land disposal; the constituents are bio-accumulable and are therefore classified as highly dangerous. Other losses of chlorinated hydrocarbons take place to the air at low levels from the reflux condensor (still), the hydrochloric acid absorber, and the chlorination reaction reflux condensor; they total slightly under 0.008 kg/kg product.

B.4 Methyl Chloroform Production Technology (Source: EPA, 1979)

In 1975, about 60% of the domestic production of this chemical was derived from vinyl chloride, almost 30% was based on the use of vinylidene chloride as raw material, and the remainder was produced by thermal chlorination of ethane.

B.4.1 Production From Vinyl Chloride--

A representative process diagram for production of methyl chloroform from vinyl chloride and chlorine is presented in Figure 3-3. The principal reactions in this process are:

$$CH_2{=}CHCl + HCl \longrightarrow C_2H_4Cl_2$$

$$C_2H_4Cl_2 + Cl_2 \xrightarrow{(400°C)} CH_3CCl_3 + HCl \text{ (by-product, reused in process)}$$

Based on 1 kg of methyl chloroform, the quantities of raw material consumed are 0.5 kg vinyl chloride, 0.525 kg chlorine, and a small quantity of ferric chloride catalyst (Gruber, 1976).

Methyl chloroform is made in two steps: (a) hydrochlorination of vinyl chloride to form 1,1-dichloroethane, and (b) thermal chlorination of the latter to produce the compound in yields greater than 95% (Lowenheim and Moran, 1975).

Vinyl chloride, recycled and make-up hydrogen chloride, recycled dichloroethane, recycled trichloroethane, and ferric chloride catalyst are fed to a tower-type reactor where a catalyzed hydrochlorination reaction between vinyl chloride and hydrogen chloride at 35 to 40°C produces dichloroethane (Gruber, 1976).

The reaction products are sent to a purification column. The dichloroethane fraction is separated as an overhead stream from the column and chlorinated (atmospheric pressure and about 400°C) with chlorine gas to produce crude trichloroethane and by-product hydrogen chloride. The crude trichloroethane, by-product hydrogen chloride, and excess dichloroethane are recycled from the chlorinator reactor to the hydrochlorinator reactor (Lowenheim and Moran, 1975).

The crude product, separated in the purification column as the high boiling fraction, is sent to a stripper column where it is steam stripped and distilled to yield purified methyl chloroform. The product yield is over 95% (Lowenheim and Moran, 1975).

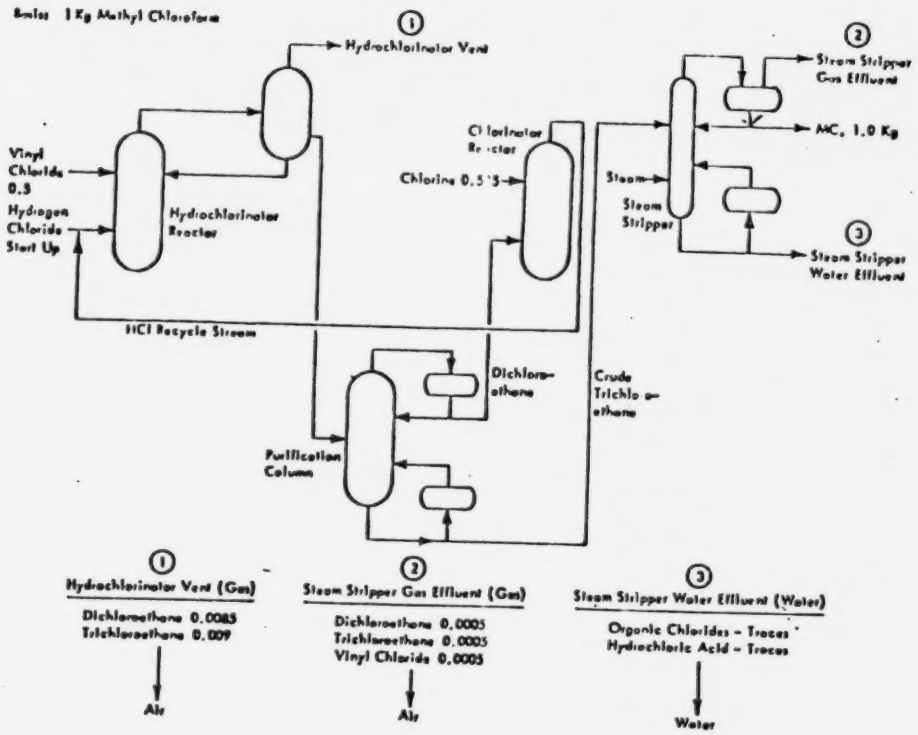


Figure B-5 Production Process for Methyl Chloroform Based on Vinyl Chloride Method (Gruber, 1975)

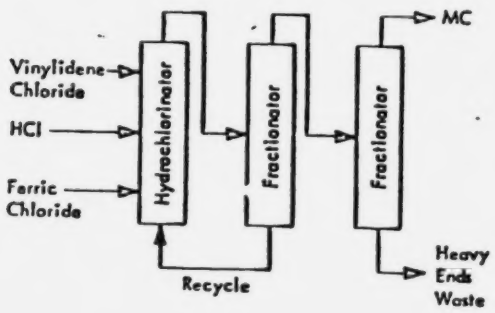
Figure B-5 shows the gas and liquid waste streams for this process; the quantities of wastes are given in kilograms of waste constituents produced per kilogram of product. The water effluent from the steam stripper contains traces of organic chlorides. Currently (1976) no land-destined hazardous wastes are discharged by this process (Gruber, 1976).

By-products and waste material are hydrogen chloride; waste gas from hydrochlorinator vent (Figure B-5 Item 1) containing 0.0085 kg of dichloroethane and 0.009 kg of trichloroethane for each kilogram of product; waste gas from steam stripper (Figure B-5 Item 2) containing 0.0005 kg each of dichloroethane, trichloroethane, and vinyl chloride for each kilogram of product; and waste water from steam stripper (Figure B-5, Item 3) containing traces of organic chlorides and hydrochloric acid.

B.4.2 Production From Vinylidene Chloride--
The basic reaction involved in this process is:

$$CH_2{=}CCl_2 + HCl \xrightarrow{FeCl_3} CH_3CCl_3$$

On the basis of 1 kg of product, the raw material requirements are 0.727 kg vinylidene chloride, 0.274 kg hydrochloric acid, and a small quantity of ferric chloride catalyst. A representative flow diagram for this process is shown in Figure A-4.



Source: Lowenheim and Moran (1975).

Figure B-4. Flow diagram for production of methyl chloroform from vinylidene chloride by hydrochlorination.

The vinylidene chloride used as raw material is obtained by: (a) chlorination of ethylene or 1,2-dichloroethane with chlorine to form 1,1,2-trichloroethane and by-product hydrogen chloride; and (b) dehydrochlorination of the 1,1,2-trichloroethane to form vinylidene chloride. The reaction of vinylidene chloride with the hydrogen chloride evolved in step (a) yields methyl chloroform (Lowenheim and Moran, 1975).

Reaction of vinylidene chloride with the by-product hydrogen chloride is ideally conducted in the liquid phase with ferric chloride as a catalyst. The chemical reaction is conducted at 25 to 35°C under slightly superatmospheric pressure. Crude product is continuously withdrawn from the hydrochlorination step and purified by fraction distillation. The purified product is treated to remove moisture and is combined with appropriate stabilizers to make the material suitable for various commercial uses. The yield of product is over 98% (Lowenheim and Moran, 1975).

No by-products are formed in this process. A heavy ends waste stream is discharged from the fractionator.

B-5 Vinylidene Chloride (Source: EPA, 1978)

The earliest and still most widely used commercial process for the production of vinylidene chloride is the treatment of 1,1,2-trichloroethane with sodium hydroxide:

$$CH_2ClCHCl_2 + NaOH \longrightarrow CH_2 = CCl_2 + NaCl + H_2O$$

1,1,2-trichloroethane can be obtained in either of two ways: chlorination of ethylene dichloride or addition of chlorine to vinyl chloride (Shelton et al., 1971). Industrially, however, large quantities of 1,1,2-trichloroethane are generally available as a by-product from the preparation of other chlorinated hydrocarbons such as ethylene dichloride. Calcium hydroxide may be substituted for the sodium hydroxide, although the caustic is better (Shelton et al., 1971), or 1,1,1-trichloroethane for 1,1,2-trichloroethane (Wessling and Edwards, 1971).

The reaction scheme is shown in Figure B-6. All equipment is fabricated from stainless steel except reboiler tubes which are nonferrous. A 10 to 20 percent by weight aqueous solution of sodium hydroxide (or a calcium hydroxide slurry) and liquid 1,1,2-trichloroethane are charged simultaneously into a heated, agitated reactor where a temperature of 60° to 100°C and 15 to 30 psi of pressure are maintained (Shelton et al., 1971). As the reaction proceeds, vinylidene chloride is distilled from the batch to prevent further cracking to acetylenic compounds. An MEHQ inhibitor is generally also added at this point. Current practices favor continuous rather than batch production.

The condenser is then purged to prevent oxygen buildup and

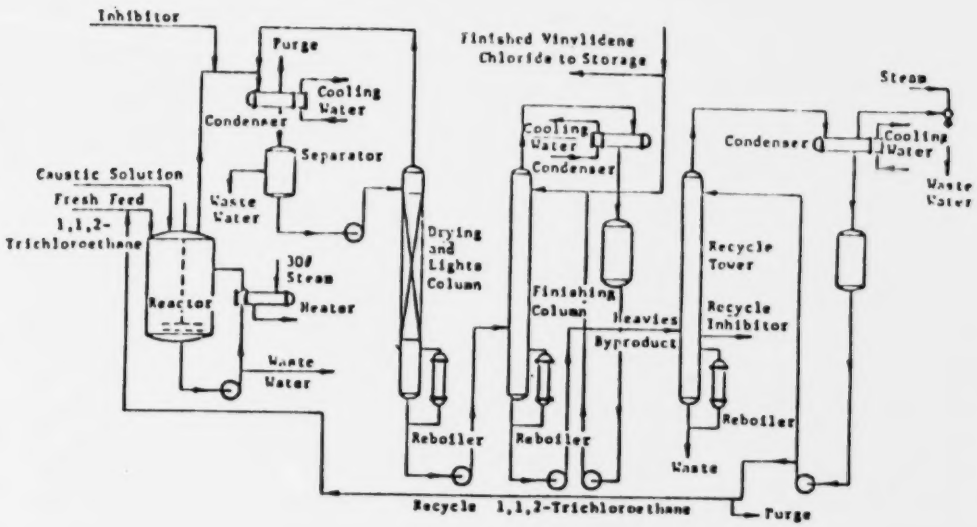
resulting peroxide formation. Water is removed after separation. The wet, inhibited vinylidene chloride is dried by azeotropic distillation and then fed to the finishing column where, under a pressure of 10 to 20 psi, the finished vinylidene chloride is withdrawn (Shelton et al., 1971). More inhibitor is added prior to storage.

The initial inhibitor, heavies and unconverted 1,1,2-trichloroethane are removed from the bottom of the finishing column and processed through the recycling tower. During recycling, waste products are removed from the bottom of the tower and the phenolic inhibitor drawn off just slightly above the bottom for recycling. The 1,1,2-trichloroethane is removed from the top of the recycling tower. After each batch is completed, a small purge of this system is also required to remove impurities which would otherwise accumulate, producing chlorinated acetylenes and, hence, an explosion hazard (Shelton et al., 1971). By the above process, if it is run continuously at 98° to 99°C, the overall yield of vinylidene chloride is approximately 90 percent (Wessling and Edwards, 1971).

Domestic production losses are estimated to result in the release of 3.355 million pounds per year of vinylidene chloride into the environment[a] (Little, 1975). The principal production losses are through vents on the purification equipment and during recycling. There is also additional monomer loss during transportation and storage.

Additional monomer may be lost during transportation and transfer to and from storage facilities. Precautions to prevent these losses are discussed briefly in Section E of this report. It is difficult to quantify these losses. However, with the use of proper handling techniques, they can be kept at a minimal level. The industries involved in vinylidene chloride monomer production are aware of the potential handling problems and are actively employing these techniques (Strasser, 1975; Dehn, 1975).

Figure B-6. PRODUCTION AND PURIFICATION OF VINYLIDENE CHLORIDE



B.6 PRODUCTION PROCESSES OF EDC (McPherson, 1979)

Direct chlorination of ethylene. Direct chlorination of ethylene to 1,2-dichloroethane is almost always conducted in a liquid phase reactor by intimately mixing ethylene and chlorine in liquid EDC. Ferric chloride, a highly efficient and selective catalyst for this reaction, is normally used in commercial processes. Amides, such as n,n-dimethylformamide, have been reported to increase PVC selectivity.[2] Oxygen, frequently present as an impurity in chlorine, likewise increases EDC selectivity in direct chlorination of ethylene by inhibition of free radical reactions that give 1,1,2-trichloroethane.

Direct chlorination reactions may be run rich in either ethylene or chlorine, depending on the methods available to the plant for handling offgases from this reactor. Conversion of the lean component is usually 100 percent, and selectivity to EDC is greater than 99 percent.

1,2-Dichloroethane, as it comes from the direct chlorination reactor, is frequently of sufficient purity for cracking, except that it may contain ferric chloride, which would lead to rapid fouling of the cracking reactor. To avoid expensive purification of this already pure EDC, one may remove $FeCl_3$ by adsorption on activated carbon[3] or other solids.[4] Alternately, one may operate the direct chlorinator at the boiling point of EDC, taking pure EDC overhead and using the heat of reaction to supply the heat for vaporization.[5,6,7,8]

Oxychlorination of ethylene to EDC. Ethylene oxychlorination is normally conducted at temperatures of 225-325° C and at pressures of one to 15 atmospheres. Catalysts for this reaction almost always contain copper chloride and sodium or potassium chloride deposited on alumina or other suitable support. The detailed mechanism of the catalyst's activity is not known, but it is recognized that cupric chloride is the active chlorinating agent. The cuprous chloride produced is rapidly reconverted to $CuCl_2$ under the reaction conditions, but the presence of some cuprous chloride is thought to be advantageous because it complexes with ethylene, bringing it into contact with $CuCl_2$ for a long enough time for chlorination to occur. The sodium or potassium chloride serves to increase EDC selectivity, mostly by inhibiting formation of ethyl chloride. Other catalyst components, such as rare earth metal chlorides, sulfate salts, ferric chloride and numerous other additives, have been described in the patent literature.

Good temperature control of the highly exothermic oxy reaction is a key element in successful production of 1,2-dichloroethane. Temperatures higher than about 325°C lead to increased byproduct formation, mostly through increased dehydrochlorination of EDC to vinyl chloride followed by additional oxychlorination to give products having high levels of chlorine substitution. High temperatures also increase the amount of ethylene burned to carbon monoxide and carbon dioxide. Of equal importance, high temperatures deactivate the catalyst by highly accelerated coking and consequent powdering of the catalyst units and by increased sublimation of copper chloride away from the catalyst.

Temperature control in fluidized bed reactors is maintained by the excellent intermixing of the catalyst particles and by use of internal cooling surfaces.[10] Temperature control in fixed bed reactors is more difficult since "hot spots" tend to develop. To keep the hot spot temperature below below 325° C, yet get maximum utilization from the reactor, it is common practice to pack the reactor tubes with active catalyst and inert diluent mixtures in proportions of each so adjusted as to have low catalyst activity at the inlet, steadily increasing to maximum activity at the outlet. This grading of the catalyst activity flattens the temperature profile, allowing for good temperature control with high productivity. For example, one patent[9] indicates the use of four zones with 93 percent, 85 percent, 40 percent, and 0 percent, respectively, of the active catalyst pellets replaced by inert graphite. As an alternate to using inert materials in the catalyst bed, catalysts, each with higher levels of $CuCl_2$ and consequently of increasing reactivity, are sometimes used.

Fluid bed oxychlorination of ethylene, operated under good control, results in 94-97 percent ethylene conversion, 95-97 percent HCl conversion, and EDC selectivities in the range of 94-96 percent. Fixed bed oxychlorinations are normally run with excess ethylene relative to HCl, resulting in 93-97 percent ethylene conversion, 94-95 percent HCl conversions, and EDC selectivities of 93-95 percent. These data do not include recovery of excess ethylene in subsequent reaction steps. Excess ethylene in vent gases from oxychlorination is normally converted to EDC by direct chlorination with chlorine,[11,12] although, if oxygen is used rather than air, the excess ethylene may be recycled directly back to oxychlorination.

Byproducts of ethylene oxychlorination are vinyl chloride, ethyl chloride, 1,1-dichloroethane, vinylidene chloride, *cis*- and *trans*-1,2-dichloroethylenes, trichloroethylene, chloroform, carbon tetrachloride, methyl chloride, methylene chloride, chloral and high boiling compounds. All of these byproducts present problems in one way or another, such that their production needs to be minimized to lower raw material costs, to lessen the difficulties of preparing pure EDC, and to prevent fouling in the cracking reactor. Chloral, in particular, needs to be removed since it polymerizes readily in strong acids to give solids which clog and foul operating lines and controls.

One must also take care to see that the feeds to oxychlorination are pure. Normally, the only problem is with low levels (0.1 to 0.5 percent) of acetylene present in the HCl from cracking of EDC. Acetylene in the feed leads to the formation of considerable highly chlorinated byproducts and tars. Selective hydrogenation of this acetylene to ethylene and ethane is practiced by many companies.[15]

Oxychlorination with oxygen instead of air. Use of oxygen instead of air for ethylene oxychlorination has received much attention.[14-19] The outstanding benefits from using oxygen are avoidance of expensive facilities to recover EDC, ethylene and other chemicals from the large nitrogen vent gas stream; a large reduction in the quantity of offgases that will probably need to be incinerated; and the ability to use ethylene as a diluent for oxychlorination, a procedure said to improve heat transfer in tubular reactors.

APPENDIX C

OCCURRENCE OF EDC IN RAW AND FINISHED WATER

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TABLE C.1 QUANTITY OF EDC IN RAW AND FINISH WATER SUPPLY

Utility number and name[a] (plant name when applicable)	Content of selected compounds in raw and finished water (ug/liter)[b]						Nonvolatile total organic carbon (mg/liter)
	1,2-Dichloroethane	Bromodichloromethane	Dibromochloromethane	Bromoform	Chloroform	Carbon tetrachloride	
1. Laurence Water Works	NF[c] NF	<0.2 9	NF 0.6	NF NF	<0.1 91	NF NF	3.7 1.6
2. Waterbury Bureau of Water (Morris Treatment Station)	NF <0.2	NF 10	NF 0.6	NF <1	NF 93	NF <2	2.2 2.9
3. Metropolitan District Commission (Norumbega Treatment Station)	NF NF	NF 0.8	NF NF	NF NF	NF 4	NF NF	2.1 2.0
4. Newport Dept. of Water (South Pond Reservoir Treatment Plant No. 1)	NF NF	NF 42	NF 13	NF 1	NF 103	NF NF	4.6 4.1
5. Dept. of Water Resources	NF NF	NF 7	NF 0.9	NF NF	NF 22	NF NF	3.0 2.5
6. Puerto Rico Aqueduct and Sewer Authority (Sergio Cuevas Water Treatment Plant)	NF NF	NF 29	NF 16	NF 2	<0.2 47	NF NF	2.0 2.0
7. Passaic Valley Water Commission	<0.1 <0.2	NF 16	NF 2	NF NF	0.3 59	<2 <2	3.6 1.9
8. Toms River Water Co.	NF NF	NF <0.8	NF 3	NF NF	0.4 0.6	NF NF	<0.05 <0.05
9. Buffalo Water Dept.	NF <0.2	NF 10	NF 4	NF NF	NF 10	NF NF	2.6 1.7
10. Village of Rhinebeck Water Dept.	3 2	NF 11	NF 4	NF NF	0.3 49	NF NF	3.5 1.6
11. Philadelphia Water Dept. (Torresdale Plant)	3 6	NF 9	NF 5	NF NF	0.2 86	NF NF	2.6 1.7
12. Wilmington Suburban Water Corp. (Stanton Plant)	NF <0.4	<0.4 11	NF 3	NF NF	0.3 23	NF <2	2.8 1.8
13. Artesian Water Co. (Llangollen Well Field Plant)	NF <0.2	NF 0.5	NF 1	NF <1	0.2 0.5	NF NF	0.05 0.2
14. Washington Aqueduct (Delacarlie Plant)	NF <0.3	NF 8	NF 2	NF NF	<0.2 41	NF NF	1.8 1.2

Source: Investigations of Selected Environmental Pollutants: 1,2 -Dichloroethane
Oak Ridge National Laboratory
EPA (1979)

TABLE C.1 QUANTITY OF EDC IN RAW AND FINISH WATER SUPPLY (cont'd.)

Utility number and name[a] (plant name when applicable)	Content of selected compounds in raw and finished water (ug/liter)[b]						Nonvolatile total organic carbon (mg/liter)
	1,2-Dichloroethane	Bromodichloromethane	Dibromochloromethane	Bromoform	Chloroform	Carbon tetrachloride	
15. Baltimore City Bureau of Water Supply (Montebello Plant No. 1)	NF NF	NF 11	NF 2	NF NF	NF 32	NF NF	1.8 1.2
16. Western Pennsylvania Water Co. (Hays Mine Plant)	NF NF	NF 2	NF 0.4	NF NF	0.3 8	NF NF	0.9 0.8
17. Strasburg Borough Water System	NF NF	NF NF	NF NF	NF NF	NF <0.1	NF NF	0.2 0.05
18. Fairfax County Water Authority (New Lorton Plant)	NF NF	<0.4 6	NF <0.6	NF NF	<0.2 67	NF NF	4.7 2.7
19. Virginia-American Water Co. Hopewell District	NF NF	NF 1	NF 0.8	NF <2	0.2 6	NF NF	4.2 0.2
20. Huntington Water Co.	<0.3 <0.4	NF 16	NF 5	NF NF	1 23	4 3	2.2 1.0
21. Wheeling Water Dept.	<0.3 <0.4	NF 28	NF 0.17	NF NF	0.2 72	NF NF	3.2 1.8
22. Miami-Dade Water and Sewer Authority (Preston Plant)	<0.2 <0.2	NF 78	NF 35	NF 3	NF 311	<2 NF	9.8 5.4
23. Jacksonville Dept. of Public Works (Highlands Pumping Station)	NF NF	NF 4	NF 2	NF NF	NF 9	NF NF	2.4 2.3
24. Atlanta Waterworks (Chattahoochee Plant)	<0.3 NF	NF 10	NF 2	NF NF	<0.2 36	NF NF	1.3 0.9
25. Owensboro Municipal Utilities	NF NF	NF 20	NF 17	NF 3	NF 13	NF NF	1.7 2.0
26. Greenville Water Dept.	NF <0.2	NF 6	NF 3	NF <1	0.3 17	NF NF	3.3 4.0
27. Tennessee American Water Co.	NF <0.4	NF 9	NF 0.7	NF NF	0.9 30	NF NF	1.1 0.6
28. Memphis Light, Gas and Water Division (Malloy Plant)	NF NF	NF 2	NF 1	NF NF	<0.2 0.9	NF NF	0.2 0.2
29. Metropolitan Water and Sewerage Dept. (Lawrence Plant)	NF NF	NF 3	NF <0.4	NF NF	<0.1 16	NF NF	1.2 0.8

TABLE C.1 QUANTITY OF EDC IN RAW AND FINISH WATER SUPPLY (cont'd.)

Utility number and name[a] (plant name when applicable)	Content of selected compounds in raw and finished water (ug/liter)[b]						Nonvolatile total organic carbon (mg/liter)
	1,2-Dichloroethane	Bromodichloromethane	Dibromochloromethane	Bromoform	Chloroform	Carbon tetrachloride	
30. Commissioners of Public Works (Stoney Plant)	NF NF	NF 9	NF 0.8	NF 0.8	<0.2 195	NF NF	11.4 4.1
31. Cincinnati Water Works	NF <0.4	NF 13	NF 4	NF NF	0.5 45	<2 <2	2.3 1.1
32. Chicago Dept. of Water and Severs (South District Water Filtration Plant), two samples	NF/NF <0.4	NF/<0.5 10	NF/NF 4	NF/NF NF	<0.2/0.4 15	NF/NF NF	1.9/1.7 1.5
33. Clinton Public Water Supply	NF NF	NF 0.5	NF NF	NF NF	<0.2 4	NF NF	7.7 6.7
34. Indianapolis Water Co. (White River Plant)	<0.3 NF	NF 8	NF <2	NF NF	0.1 31	NF 2	5.1 2.6
35. Whiting Water Dept. After pre Cl; Before pre Cl;	NF NF NF	11 <0.8 0.3	3 NF NF	NF NF NF	16 0.1 0.5	NF NF NF	2.0 1.9 1.5
36. Detroit Metro Water Dept. (Waterworks Park Plant)	0.5 0.4	NF 9	NF 3	NF NF	<0.2 12	NF NF	2.6 1.2
37a. Mt. Clemens Water Purification	NF <0.4	NF 6	NF <2	NF NF	NF 11	NF NF	2.0 1.4
37b. Mt. Clemens Water Purification (after replacement of granular activated carbon)	<0.2 NF	NF 3	NF <2	NF NF	0.9 6	NF NF	6.7 1.4
38. St. Paul Water Authority	NF NF	NF 7	NF 2	NF NF	<0.2 44	NF NF	7.9 4.4
39. Cleveland Division of Water (Division Filtration Plant)	NF NF	NF 9	NF 4	NF NF	NF 18	NF NF	2.2 1.8
40. City of Columbus (Dublin Road Plant)	NF NF	NF 8	NF <0.4	NF NF	0.1 134	NF NF	6.8 2.3
41. Dayton Water Works (Ottawa Plant)	<0.2	NF 8	NF 11	NF 4	NF 8	NF <2	0.9 0.7

TABLE C.1 QUANTITY OF EDC IN RAW AND FINISH WATER SUPPLY (cont'd.)

Utility number and name[a] (plant name when applicable)	Content of selected compounds in raw and finished water (µg/liter)[b]						Nonvolatile total organic carbon (mg/liter)
	1,2-Dichloroethane	Bromodichloromethane	Dibromochloromethane	Bromoform	Chloroform	Carbon tetrachloride	
42. Indian Hill Water Supply	NF	NF	NF[c]	NF	<0.2	NF	0.8
	NF	7	11	NF	5	NF	0.9
43. Piqua Water Supply	NF	NF	NF	NF	NF	NF	6.0
	<0.2	13	3	NF	131	NF	4.2
44. Mahoning Valley Sanitation District	NF	NF	NF	NF	NF	NF	4.7
	NF	5	<1	NF	80	NF	3.1
45. Milwaukee Water Works (Howard Avenue Purification Plant)	NF	NF	NF	NF	<0.2	NF	2.4
	<0.2	7	3	NF	9	NF	1.7
46. Oshkosh Water Utility	NF	NF	NF	NF	NF	NF	4.5
	<0.2	4	<0.4	NF	26	NF	3.3
47. Terrebonne Parish Waterworks (District No. 1)	NF	NF	NF	NF	NF	NF	5.6
	0.2	32	8	<1	134	NF	3.2
48. Camden Municipal Water Works	NF	NF	NF	NF	NF	NF	3.1
	NF	19	7	NF	40	NF	1.5
49. Town of Logansport Water System	NF	NF	NF	NF	0.7	NF	3.3
	NF	39	24	3	28	NF	3.5
50. City of Albuquerque	NF	NF	NF	NF	NF	NF	<0.05
	NF	1	2	3	0.4	NF	<0.05
51. Oklahoma City Water Dept. (Hefner Plant)	NF	NF	NF	NF	NF	NF	3.6
	<0.4	28	20	6	44	<2	2.8
52. Brownsville Public Utility Board (Plant No. 2)	NF	NF	NF	NF	NF	NF	6.7
	NF	37	100	92	12	NF	3.1
53. Dallas Water Utilities (Bachman Plant)	NF	NF	NF	NF	<0.1	NF	3.4
	NF	4	<2	NF	18	NF	2.9
54. San Antonio City Water Board	NF	NF	NF	NF	NF	NF	0.5
	NF	0.9	3	3	0.2	NF	0.5
55a. Ottumwa Waterworks (2/17/75)	NF	NF	NF	NF	<0.2	NF	4.1
	NF	NF	NF	NF	0.8	NF	2.3
55b. Ottumwa Waterworks (4/7/75)	NF	NF	NF	NF	NF	NF	4.9
	NF	NF	NF	NF	1	NF	2.4

TABLE C.1 QUANTITY OF EDC IN RAW AND FINISH WATER SUPPLY (cont'd.)

Utility number and name[a] (plant name when applicable)	Content of selected compounds in raw and finished water (ug/liter)[b]						Nonvolatile total organic carbon (mg/liter)
	1,2-Dichloroethane	Bromodichloromethane	Dibromochloromethane	Bromoform	Chloroform	Carbon tetrachloride	
56. Clarinda Iowa Water Works	NF	NF	NF	NF	<0.2	NF	3.5
	NF	19	4	NF	48	NF	3.0
57. Davenport Water Co.	NF	NF	NF	NF	0.4	NF	6.5
	<0.4	8	<0.6	NF	88	NF	4.4
58. Topeka Public Water Supply (South Plant)	NF	<0.8	NF	NF	0.4	NF	3.4
	NF	38	19	5	88	3	2.2
59. Missouri Utility Co.	0.2	NF	NF	NF	0.2	NF	4.5
	0.3	21	2	NF	116	2	3.6
60. Kansas City (Mo.) Water Dept.	NF	NF	NF	NF	NF	NF	3.4
	NF	8	2	NF	24	NF	1.9
61. St. Louis County Water Co. (Central Plant)	0.3	NF	NF	NF	NF	NF	3.4
	0.4	13	3	<1	55	NF	2.6
62. Lincoln Municipal Water Supply	NF	NF	NF	NF	NF	NF	1.4
	NF	6	4	<2	4	NF	1.4
63. City Water Dept.	NF	NF	NF	NF	NF	NF	9.2
	NF	1	NF	NF	3	NF	5.2
64. Denver Water Board (Moreton Plant)	NF	NF	NF	NF	<0.2	NF	2.8
	NF	10	3	NF	14	NF	1.7
65. Pueblo Board of Waterworks (Gardner Plant)	NF	NF	NF	NF	<0.2	NF	1.8
	NF	2	<2	NF	2	NF	1.6
66. Huron Water Dept.	NF	NF	NF	NF	NF	NF	19.2
	NF	116	49	8	309	NF	12.2
67. Salt Lake Water Dept.	<0.4	NF	NF	NF	0.2	NF	1.2
	NF	14	8	NF	20	NF	0.9
68. City of Tucson Water and Sewers Dept. (Plant No. 1)	NF	NF	NF	NF	<0.1	NF	<0.05
	NF	<0.8	2	13	<0.2	NF	<0.05
69. City of Phoenix Water and Sewers Dept. (Verde Plant)	NF	NF	NF	NF	<0.2	NF	1.0
	NF	15	17	<4	9	NF	1.0

TABLE C.1 QUANTITY OF EDC IN RAW AND FINISH WATER SUPPLY (cont'd.)

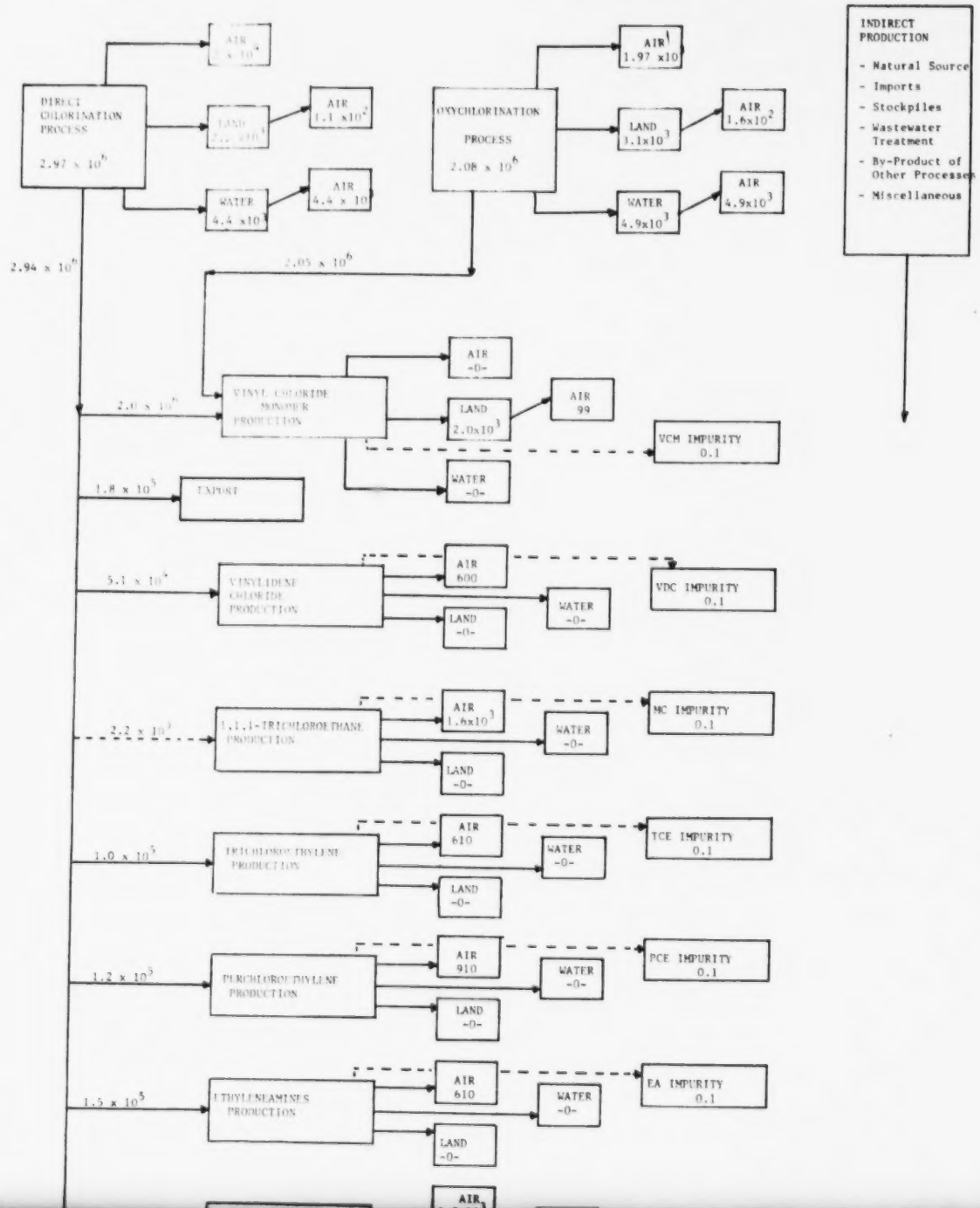
Utility number and name[a] (plant name when applicable)	Content of selected compounds in raw and finished water (ug/liter)[b]						Nonvolatile total organic carbon (mg/liter)
	1,2-Dichloroethane	Bromodichloromethane	Dibromochloromethane	Bromoform	Chloroform	Carbon tetrachloride	
70. Dept. of Supply and Purification	NF[c]	NF	NF	NF	<0.2	NF	3.7
	NF	17	15	2	16	NF	2.4
71. Contra Costa County Water Dept. (Bollman Plant)	NF	<0.3	NF	NF	0.3	NF	3.4
	NF	18	6	<1	31	NF	1.9
72. City of Dos Palos Water Dept.	NF	NF	NF	NF	NF	NF	4.4
	NF	53	34	7	61	NF	2.9
73. Los Angeles Dept. of Water and Power	NF	NF	NF	NF	<0.1	NF	1.2
	NF	6	3	NF	32	NF	1.3
74. San Diego Water Utilities Dept. (Miramar Plant)	NF	NF	NF	NF	NF	NF	2.9
	NF	30	19	3	52	NF	2.8
75. San Francisco Water Dept. (San Andreas Treatment Plant)	NF	NF	NF	NF	NF	NF	1.3
	NF	15	4	<0.8	41	NF	1.6
76. Seattle Water Dept. (end of distribution system)	NF	NF	NF	NF	<0.2	NF	0.9
	NF	0.9	NF	NF	15	NF	0.9
77. Douglas Water System	NF	NF	NF	NF	NF	NF	3.4
	NF	0.8	<0.4	NF	40	NF	2.8
78. Idaho Falls Water Dept.	NF	NF	NF	NF	<0.2	NF	0.5
	NF	3	3	[illegible]	4	NF	0.3
79. City of Corvallis Utilities Division (Taylor Plant)	NF	NF	NF	NF	NF	NF	1.0
	NF	3	NF	NF	26	NF	0.4
80. Ilwaco Municipal Water Dept.	NF	NF	NF	NF	0.1	NF	7.5
	NF	35	5	NF	167	NF	3.1
Range	NF-3	NF-0.8	NF	NF	NF-0.9	NF-4	<0.05-19.2
	NF-6	NF-116	NF-100	NF-92	<0.1-311	NF-3	<0.05-12.2

[a] See Table 17 for location of utility.
[b] First line indicates raw-water data; second line indicates finished-water data.
[c] NF = none found.

Source: Adapted from Symons et al., 1975, Table 5, pp. 640-641. Reprinted with permission of the American Water Works Association from JOURNAL AWWA Volume 67, copyrighted 1975.

APPENDIX D

FLOW DIAGRAM OF EDC


INDIRECT PRODUCTION
- Natural Source
- Imports
- Stockpiles
- Wastewater Treatment
- By-Product of Other Processes
- Miscellaneous
DIRECT CHLORINATION PROCESS
2.97 x 10^6
AIR
LAND
AIR 1.1 x10^2
WATER 4.4 x10^3
AIR
OXYCHLORINATION PROCESS
2.08 x 10^6
AIR 1.97 x10^1
LAND 3.1x10^3
AIR 1.6x10^2
WATER 4.9x10^3
AIR 4.9x10^3
2.94 x 10^6
2.05 x 10^6
VINYL CHLORIDE MONOMER PRODUCTION
AIR -0-
LAND 2.0x10^3
AIR 99
WATER -0-
VCM IMPURITY 0.1
1.8 x 10^5
EXPORT
VINYLIDENE CHLORIDE PRODUCTION
AIR 600
WATER -0-
LAND -0-
VDC IMPURITY 0.1
1,1,1-TRICHLOROETHANE PRODUCTION
AIR 1.6x10^3
WATER -0-
LAND -0-
MC IMPURITY 0.1
TRICHLOROETHYLENE PRODUCTION
AIR 610
WATER -0-
LAND -0-
TCE IMPURITY 0.1
PERCHLOROETHYLENE PRODUCTION
AIR 910
WATER -0-
LAND -0-
PCE IMPURITY 0.1
ETHYLENEAMINES PRODUCTION
AIR 610
WATER -0-
LAND -0-
EA IMPURITY 0.1

D-1

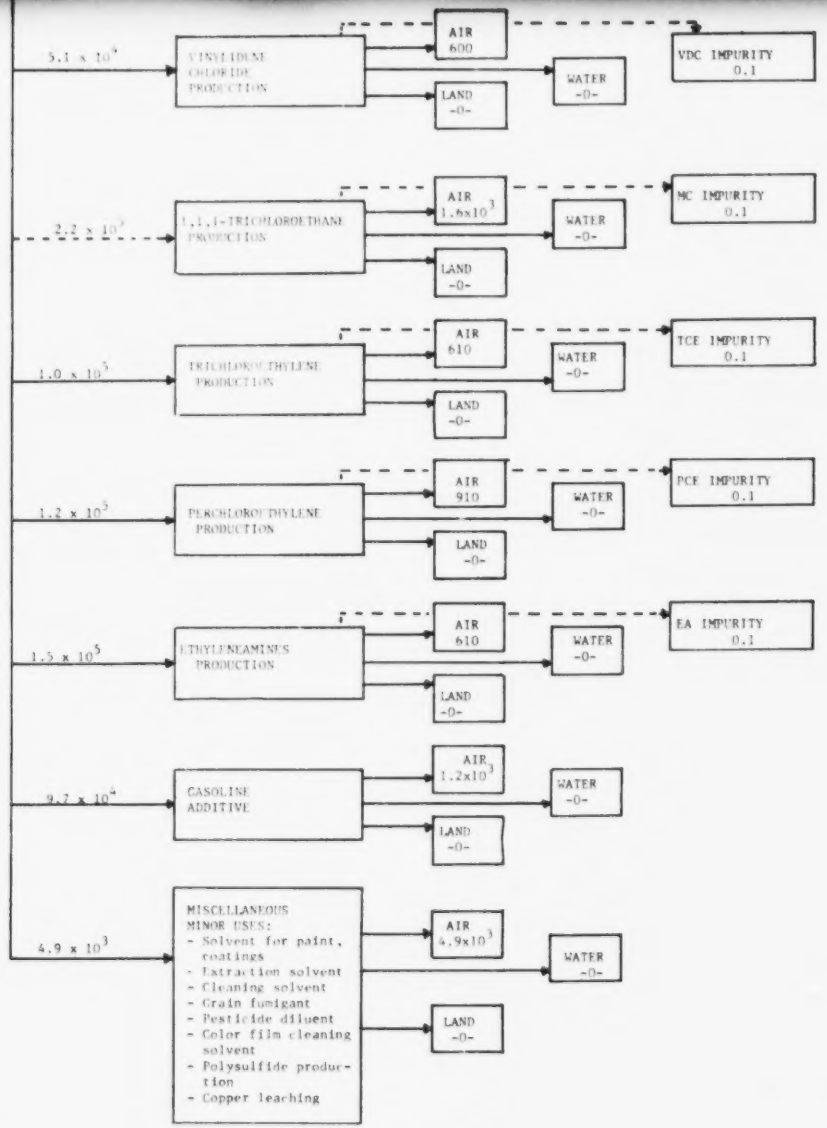


FIGURE D.1 ENVIRONMENTAL FLOW DIAGRAM OF EDC